PB84-110576

# Proceedings of Symposium on Flue Gas Desulfurization, Hollywood, Florida May 17-20, 1982. Volume 1 Session 1 through Session 6

Research Triangle Inst.
Research Triangle Park, NC

Oct 83

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-110576

EPA-600/9-83-020a
October 1983

# PROCEEDINGS: SYMPOSIUM ON FLUE GAS DESULFURIZATION
## Volume 1

Hollywood, Florida
May 17-20, 1982

by
Franklin A. Ayer, Compiler
Research Triangle Institute
Cornwallace Road
Research Triangle Park, NC 27709

EPA Contract 68-02-3170

EPA Project Officer
Julian W. Jones

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

445

## TECHNICAL REPORT DATA
*(Please read Instructions on the reverse before completing)*

| | | |
|---|---|---|
| 1. REPORT NO.<br>EPA-600/9-83-020a | 2. | 3. RECIPIENT'S ACCESSION NO.<br>PB84 110576 |
| 4. TITLE AND SUBTITLE<br>Proceedings: Symposium on Flue Gas Desulfurization, Hollywood, FL, May 1982; Volume 1. Session 1 thru Session 6 | | 5. REPORT DATE<br>October 1983 |
| | | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S)<br>Franklin A. Ayer, Compiler | | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Research Triangle Park<br>P.O. Box 12194<br>Research Triangle Park, North Carolina 27709 | | 10. PROGRAM ELEMENT NO. |
| | | 11. CONTRACT/GRANT NO.<br>68-02-3170, Task 60 |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>EPA, Office of Research and Development *<br>Industrial Environmental Research Laboratory<br>Research Triangle Park, NC 27711 | | 13. TYPE OF REPORT AND PERIOD COVERED<br>Proceedings; 5/17-20/82 |
| | | 14. SPONSORING AGENCY CODE<br>EPA/600/13 |

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Julian W. Jones, Mail Drop 61, 919/541-2489. The Electric Power Research Institute cosponsored the symposium.

16. ABSTRACT

The proceedings, in two volumes, document presentations at the Seventh Symposium on Flue Gas Desulfurization (FGD), held in Hollywood, FL, May 17-20, 1982. The Symposium was cosponsored by EPA's Industrial Environmental Research Laboratory, Research Triangle Park (IERL-RTP), NC, and EPRI's Coal Combustion Systems Division, Palo Alto, CA. Presentations covered subjects such as air quality and solid waste regulations, commercial applications of FGD technology, materials of construction, reliability and maintenance, combined SOx/NOx removal, FGD by-product disposal/utilization, and dry FGD systems development.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group | |
|---|---|---|---|---|
| Pollution | Nitrogen Oxides | Pollution Control | 13B | 07B |
| Flue Gases | Sulfur Oxides | Stationary Sources | 21B | |
| Desulfurization | Waste Disposal | Solid Waste | 07A,07D | |
| Coal | Circulation | | 21D | 14G |
| Reliability | Waste Water | | 14D | |
| Maintenance | | | 15E | |

| | | |
|---|---|---|
| 18. DISTRIBUTION STATEMENT<br>Release to Public | 19. SECURITY CLASS *(This Report)*<br>Unclassified | 21. NO. OF PAGES<br>447 |
| | 20. SECURITY CLASS *(This page)*<br>Unclassified | 22. PRICE |

EPA Form 2220-1 (9-73)

## NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

# ABSTRACT

These proceedings are of the Symposium on Flue Gas Desulfurization, held May 17 to 20, 1982, in Hollywood, Florida. The symposium was sponsored by EPA's Industrial Environmental Research Laboratory, located in Research Triangle Park, North Carolina, and the EPRI Coal Combustion Systems Division, located in Palo Alto, California.

The objective of the symposium was to provide a forum for supplier, user, service, and regulatory groups to discuss the technical and regulatory aspects of $SO_2$ control. The primary emphasis was on progress in $SO_2$ control technology, recent experience, and test results, not on future plans. The organization of sessions was as follows:

- Day 1
  --Opening session
  --Materials of construction
- Day 2
  --Dual alkali
  --Special studies (chemistry, continuous emission monitoring, characterization, etc.)
  --Evening panel on reliability and maintenance
- Day 3
  --Combined $SO_x/NO_x$
  --Limestone/organic acid
  --Utility applications and by-products
- Day 4
  --Dry flue gas desulfurization

Volume 1 contains 22 papers from Days 1, 2, and 3 plus abstracts from panel members. Volume 2 contains 13 papers from Days 3 and 4 plus eight unpresented papers.

# PREFACE

These proceedings for the Symposium on Flue Gas Desulfurization constitute the final report submitted to EPA's Industrial Environmental Research Laboratory, Research Triangle Park (IERL-RTP), North Carolina, and to the Coal Combustion Systems Division, EPRI, Palo Alto, California. The symposium was conducted at The Diplomat Hotel in Hollywood, Florida, May 17 to 20, 1982.

This symposium was designed to provide a forum for the exchange of technical developments and regulatory information on the systems and processes that are applicable to utility and industrial boilers. In the opening session, a keynote address was given on the assessment of forecasts for electrical energy demand and coal for power generation; presentations were made on the status of air quality legislation and regulations, the status of solid waste regulations, trends in commercial application of flue gas desulfurization (FGD) technology, and an economic comparison of alternative limestone scrubbing options. There were subsequent technical sessions on materials of construction, dual-alkali FGD, special studies, reliability and maintenance (a panel discussion), flue gas treatment (combined $SO_x/NO_x$) removal, limestone/organic acid, lime-limestone utility applications, byproduct disposal and utilization, and dry FGD systems. Participants represented electric utilities, equipment and process suppliers, state environmental agencies, coal and petroleum suppliers, EPA and other federal agencies, and research organizations.

The following persons contributed their efforts to this symposium:

- Michael A. Maxwell, Chief, Emissions/Effluent Technology Branch, Utilities and Industrial Power Division, IERL-RTP, Research Triangle Park, North Carolina, acted as a symposium chairman.

- Stuart M. Dalton, Program Manager, Desulfurization Processes Program, Coal Combustion Systems Division, EPRI, Palo Alto, California, acted as a symposium chairman and was the EPRI project manager.

- Julian W. Jones acted as the symposium program chairman and was the EPA project officer.

- Franklin A. Ayer, Manager, Conference Planning Office, Center for Technology Applications, Research Triangle Institute, Research Triangle Park, North Carolina, was symposium coordinator and compiler of the proceedings.

Preceding page blank

## TABLE OF CONTENTS

VOLUME 1 Page

Session 1: OPENING SESSION. . . . . . . . . . . . . . . . . . . . . . . . . 1
Michael A. Maxwell and Stuart M. Dalton, Chairmen

Keynote Address: Kilowatts from Coal. . . . . . . . . . . . . . . . . . . . 2
H. W. Elder

Status of Air Quality Legislation/Regulations. . . . . . . . . . . . . . . 20
Walter C. Barber

Status of Solid Waste Regulations. . . . . . . . . . . . . . . . . . . . . 20
Stephen A. Lingle

Trends in Commercial Application of FGD Technology . . . . . . . . . . . 21
B. A. Laseke, Jr.,* M. T. Melia, and N. G. Bruck

Economic Evaluation and Comparison of Alternative Limestone Scrubbing Options. . . . . . . . . . . . . . . . . . . . . . . 50
T. A. Burnett, R. L. Torstrick,* and F. A. Sudhoff

Session 2: MATERIALS OF CONSTRUCTION . . . . . . . . . . . . . . . . . . 73
Charles E. Dene, Chairman

Materials Problem: Operating a Closed-Loop Limestone FGD System . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 74
Daniel A. Froelich* and Marcus W. Ware

Fiberglass Reinforced Plastics and Their Successful Use in Flue Gas Desulfurization Equipment. . . . . . . . . . . . . . . 85
Winston J. Renoud* and Richard J. Lewandowski

Full-Scale DAFGD Experience at Central Illinois Public Service Company's Newton Station . . . . . . . . . . . . . . . . . . . . . . .115
R. J. Grant* and J. L. Simpson

Laboratory and Field Evaluation of Materials for Flue Gas Desulfurization Systems. . . . . . . . . . . . . . . . . . . . . . . .122
G. H. Koch* and J. A. Beavers

Materials of Construction Problems at Pleasants Power Station. . . . . . . . . . . . . . . . . . . . . . . . . . . . .141
W. R. Cress* and T. L. Misner

*Denotes speaker

Preceding page blank

Page

Session 3: DUAL ALKALI . . . . . . . . . . . . . . . . . . . . . . . . . . 149
Norman Kaplan, Chairman

Results of the DOWA Technology Tests at the Shawnee Scrubber Facility . . . . . . . . . . . . . . . . . . . . . . . . . . 150
G. Hollinden,* R. Runyan, S. Newton, F. Garrison, S. Pfeffer, and D. Smith

Full-Scale Dual Alkali FGD Demonstration at Louisville Gas and Electric Company . . . . . . . . . . . . . . . . . . . . . . . . . . 162
Norman Kaplan,* Elizabeth D. Gibson, and Lawrence R. Woodland

Double Alkali Flue Gas Desulfurization Retrofit on an Industrial Cogeneration Facility . . . . . . . . . . . . . . . . . 183
D. V. Francis,* R. J. Biolchini, and J. D. Coons

Pilot Testing of Limestone Regeneration in Dual Alkali Processes . . . . . . . . . . . . . . . . . . . . . . . . . . 201
John C. S. Chang, J. H. Dempsey,* and Norman Kaplan

Session 4: SPECIAL STUDIES . . . . . . . . . . . . . . . . . . . . . . . . . . 223
Dorothy A. Stewart, Chairman

Chloride Ion Effects on Limestone FGD System Performance . . . . . . . 224
John C. S. Chang* and Dennis Laslo

FGD Chemistry and Water Integration . . . . . . . . . . . . . . . . . . . 255
Dorothy A. Stewart* and O. W. Hargrove

Continuous Emission Monitoring of Flue Gas Desulfurization Systems . . . . . . . . . . . . . . . . . . . . . . . . . . 269
Peter R. Westlin

Full-Scale Utility Flue Gas Desulfurization System Characterization Results . . . . . . . . . . . . . . . . . . . . . 284
Richard G. Rhudy, Wayne E. Morgan,* Earl O. Smith, and Philip S. Lowell

PANEL: RELIABILITY AND MAINTENANCE . . . . . . . . . . . . . . . . . . . . 313
Thomas M. Morasky, Chairman

How Reliable Should an FGD System Be? . . . . . . . . . . . . . . . . . . 314
David W. Joos

Failure Mode Analysis for Lime/Limestone FGD Systems . . . . . . . . . 315
Harvey S. Rosenberg

Reliability of Lime/Limestone FGD Technology . . . . . . . . . . . . . 316
Bernard A. Laseke

*Denotes speaker

Page

Flue Gas Desulfurization Reliability Improvement at the Bruce Mansfield Plant. . . . . . . . . . . . . . . . . . . . . . . . .317
Russell C. Forsythe

Positive Thoughts About FGD Reliability. . . . . . . . . . . . . . . . . .317
James H. Buckner

Design Features of a Highly Reliable FGD System. . . . . . . . . . . .318
Christopher P. Wedig

Session 5: FLUE GAS TREATMENT (COMBINED $SO_x/NO_x$) REMOVAL. . . . . . . .319
J. David Mobley, Chairman

$SO_x$ and $NO_x$ Removal for Coal-Fired Boilers in Japan. . . . . . . . . . .320
Jumpei Ando

EPA's Pilot Plant Evaluations of $NO_x$ and $NO_x/SO_x$ Flue Gas Treatment Technology . . . . . . . . . . . . . . . . . . . . . . . . .341
J. David Mobley and Jack M. Burke*

DOE's Electron Beam Irradiation Developmental Program. . . . . . . . .359
Edward C. Trexler

Session 6: LIMESTONE/ORGANIC ACID . . . . . . . . . . . . . . . . . . . . . .375
J. David Mobley, Chairman

Buffer Additives for Limestone Scrubbing: A Review of R&D Results. . . . . . . . . . . . . . . . . . . . . . . . . . . . . .376
Gary T. Rochelle

Results of Industrial and Utility Boiler Full-Scale Demonstration of Adipic Acid Addition to Limestone Scrubbers . . . . .400
J. D. Colley, O. W. Hargrove,* and J. David Mobley

Commercial Application Experience With Organic Acid Addition at City Utilities of Springfield. . . . . . . . . . . . . . .425
N. D. Hicks* and D. M. Fraley

VOLUME 2

Session 7: LIME/LIMESTONE UTILITY APPLICATIONS. . . . . . . . . . . . . .437
Charles C. Masser, Chairman

Flue Gas Desulfurization Operations at Apache Station. . . . . . . . .438
Robert L. Maurice, Jr.

*Denotes speaker

Page

Evaluation of Alternative FGD System Removal Efficiency and Reliability Improvement Options at Arizona Public Service Company's Four Corners Units 1, 2, and 3 . . . . . . . . . . . . . . . . . . .448
D. W. Joos,* W. E. Morgan, J. G. Noblett, and C. D. Allen

Session 8: BY-PRODUCT DISPOSAL/UTILIZATION . . . . . . . . . . . . . . . .469
Julian W. Jones, Chairman

Characterization and Environmental Evaluation of Full-Scale Utility Waste Disposal Sites - March 1982 Status Report. . . . . . . .470
C. J. Santhanam,* C. B. Cooper, A. A. Balasco, and J. W. Jones

Summary of EPRI FGD Sludge Disposal Research . . . . . . . . . . . . . .492
Dean M. Golden

Utilization of FGD By-Product Gypsum . . . . . . . . . . . . . . . . . . .509
Stephen D. Jenkins* and William Ellison

Characteristics of Waste Products from Dry Scrubbing Systems. . . . . . . . . . . . . . . . . . . . . . . . . . .526
Carol May Thompson* and Richard G. Rhudy

Session 9: DRY FGD SYSTEMS . . . . . . . . . . . . . . . . . . . . . . . .549
James D. Kilgroe, Chairman

Current Status of Dry $SO_2$ Control Systems. . . . . . . . . . . . . . . . . . .550
Mary E. Kelly,* James D. Kilgroe, and Theodore G. Brna

Dry FGD Pilot Plant Results: Lime Spray Absorption for High Sulfur Coal and Dry Injection of Sodium Compounds for Low Sulfur Coal. . . . . . . . . . . . . . . . . . . . . . . . . . . . . .574
Eric A. Samuel,* Thomas W. Lugar, Dennis E. Lapp,
Owen F. Fortune, Theodore G. Brna, and Ronald L. Ostop

EPRI Spray Drying Pilot Plant Status and Results . . . . . . . . . . .595
Gary M. Blythe, John M. Burke, Mary E. Kelly,
Larry A. Rohlack, and Richard G. Rhudy
(Presented by Stuart M. Dalton and Gary M. Blythe)

Demonstration of $SO_2$ Removal on a Coal-Fired Boiler by Injection of Dry Sodium Compounds. . . . . . . . . . . . . . . . . . .628
L. J. Muzio, T. W. Sonnichsen,* R. G. Hooper,
G. P. Green, H. G. Brines, and N. D. Shah

Dry Scrubbing at Northern States Power Company Riverside Generating Plant . . . . . . . . . . . . . . . . . . . . . . . . . . . . .650
Steven M. Kaplan, Yang-Jen Chen, Robert C. Hyde,
Carl A. Sannes, Jr.,* and Michael F. Skinner

*Denotes speaker

Page

Atomization - The Key to Dry Scrubbing at the Coyote Station . . . . .673
M. F. Lewis* and D. C. Gehri

$SO_2$ Control with Limestone in Low $NO_x$ Systems: Development Status . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .689
D. C. Drehmel,* G. B. Martin, and J. H. Abbott

UNPRESENTED PAPERS . . . . . . . . . . . . . . . . . . . . . . . . .713

Pilot Plant Evaluation of By-Product Dibasic Acids as Buffer Additives for Limestone Flue Gas Desulfurization Systems . . . . . . .714
John C. S. Chang and J. H. Dempsey

Dry Flue Gas Desulfurization End-Product Disposal Riverside Demonstration Facility Experience. . . . . . . . . . . . . . . . . . . .734
James R. Donnelly, Richard P. Ellis, and William C. Webster

Recent Operating Results with the Double Alkali Process. . . . . . . .751
Thomas H. Durkin, James H. Wilhelm, and Willard L. Boward, Jr.

A Proven Reagent for High Sulfur Coal Flue Gas Desulfurization . . . .765
David S. Henzel and Donald H. Stowe

Simultaneous Removal of $SO_2$ and Particulates from Flue Gas . . . . . .782
William M. Nelms

Heavy Metals Removal from Double Alkali Waste - Makes Waste Product Usable . . . . . . . . . . . . . . . . . . . . . . . .797
Marcus A. Mulkey

The Selection and Use of Alloys for Flue Gas Desulfurization Systems. . . . . . . . . . . . . . . . . . . . . . . . . .802
W. L. Silence, P. E. Manning, and A. I. Asphahani

Experimental Evaluation of Spray Dryer Flue Gas Desulfurization for Use with Eastern U.S. Coals. . . . . . . . . . . .821
J. T. Yeh, R. J. Demski, D. F. Gyorke, and J. I. Joubert

APPENDIX: Attendees . . . . . . . . . . . . . . . . . . . . . . . .841

*Denotes speaker

## Session 1: OPENING SESSION

Michael A. Maxwell, Chairman
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

Stuart M. Dalton, Chairman
Electric Power Research Institute
Palo Alto, CA

# KILOWATTS FROM COAL

by: H. W. Elder
Division of Energy Demonstrations and Technology
Office of Power
Tennessee Valley Authority
Muscle Shoals, Alabama 35660

## ABSTRACT

An assessment of forecasts for electrical energy demand and the coal for power generation is presented. Some factors that influence coal use, including flue gas desulfurization (FGD) and alternative control technology, are discussed. Performance and reliability are more important than ever.

## INTRODUCTION

Many factors influence both the need for electric generation capacity and the way in which the load is produced. Utility planners must estimate future peak demand and load factors for the system many years before new capacity can be brought online because the lead time for permitting, design, procurement, and installation of base-load facilities has stretched to 10 years or more. During the period between initiation and completion of a project numerous things can change.

Projections made in 1972 and in 1980 for electric generation capacity in 1990 are shown in Figure 1. During that 8-year period the estimated total need was reduced by about one-third. The nuclear forecast changed drastically and the projected use of coal substantially decreased. What happened to change the projections?

Prior to the oil embargo in 1973, electricity prices were stable and national comsumption was increasing at about 7% annually, a rate that doubles the demand in 10 years. In the 1950s and 1960s, economy of scale and other efficiencies caused electricity produced from coal in new plants to be cheaper than that produced in older facilities and expansion was cost effective. In the early 1970s, the industry began major commitments to nuclear plants for new capacity based largely on historical growth rates.

After the oil embargo, rapidly increasing fuel costs, high inflation, and incredible interest rates drove up both capital and operating costs. Between 1973 and 1980, the national average price of electricity increased by 38%. Old capacity began to look like a real bargain compared with new capacity and conservation began to play a major role. Some producers of electric power instituted active programs to encourage more efficient use.

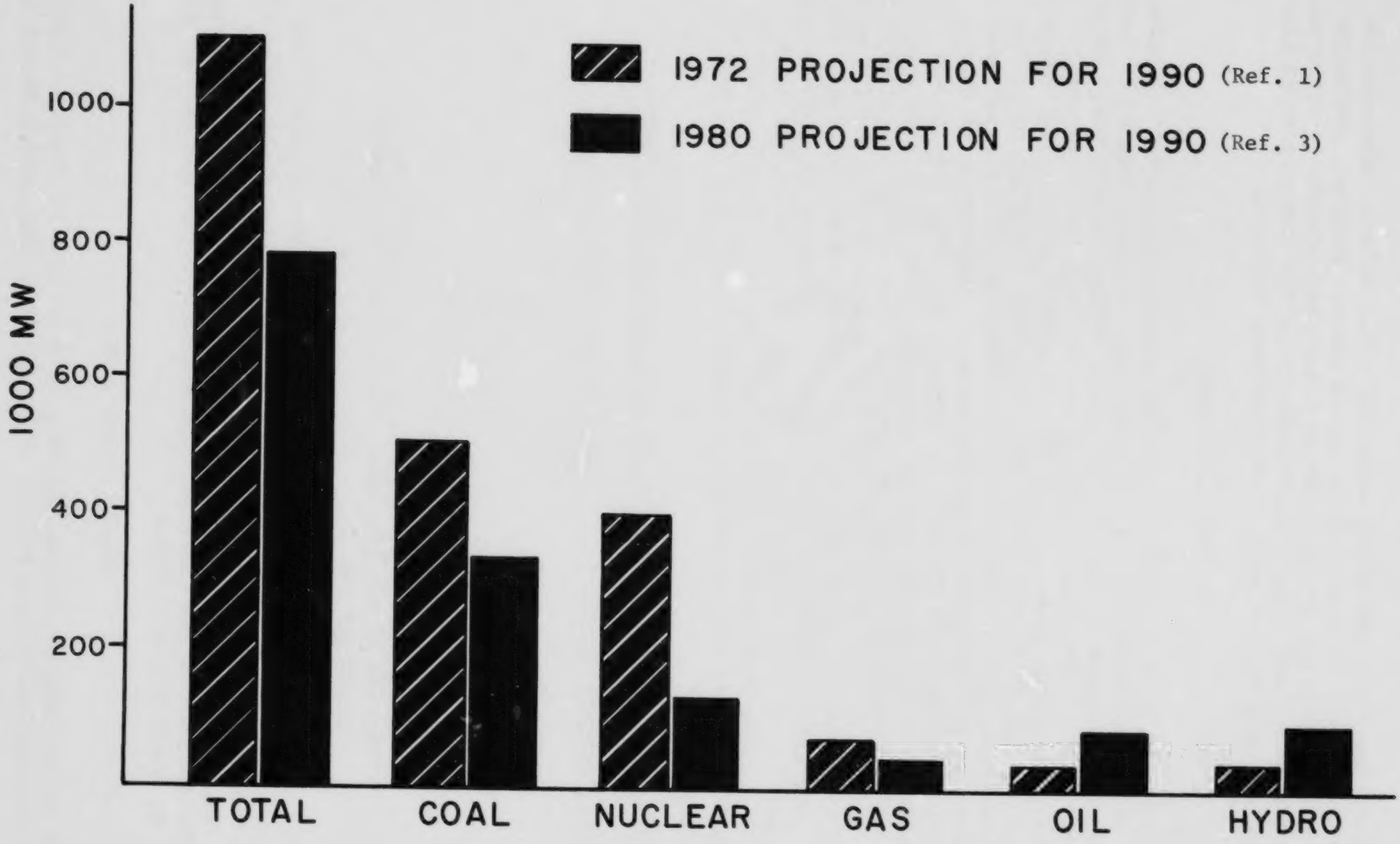


Figure 1. Projected 1990 electric generating capacity.

Preceding page blank

For example, the Tennessee Valley Authority (TVA) offered interest-free loans for insulation of electrically heated homes. However, increasing price of electricity was probably the most important factor in conservation by both residential and industrial consumers and the industry found that the market was much more elastic than previously believed.

## TVA LOAD GROWTH

The inherent risk in load forecasting is painfully evident in Table 1. In 1974, TVA anticipated that by the year 2000, the peak load would reach 68,000 MW and a program to install 17 nuclear units was underway. During subsequent years as the demand forecast was reduced, the construction programmed was trimmed back. At present, 5 units are operating, construction is proceeding on 4, and 8 have been deferred. In addition to the factors that have affected other utilities, TVA has had a further complication because it provides electrical energy to the Department of Energy (DOE) for processing nuclear fuel. As the national need for nuclear plants decreased, DOE power requirements for processing fuel diminished and planned TVA nuclear plants to supply the power were not needed as quickly--a Catch 22 situation. The historical and projected loads for the TVA system are shown in Figure 2. From 1976 on, the load has been about level and it actually decreased in 1979-80. The forecast is based on an annual increase of 0.3%, 2.0%, and 2.5%, respectively, for the low, medium, and high levels. The difference between the high and low value is equivalent to about 10,000 MW. TVA expects to have capacity to meet the high growth rate.

TABLE 1. TVA ESTIMATES OF PEAK LOAD IN YEAR 2000*

| Year of forecast | Load in year 2000 (1000 MW) |
|---|---|
| 1974 | 68 |
| 1977 | 62 |
| 1979 | 40 |
| 1982 | 33 |

*"Review of the TVA Load Growth/Plant Construction Situation" (2).

The nuclear program also affects coal consumption. Figure 3 shows the historical and projected coal burn. Prior to 1981, over 30 million tons of coal produced about 80 billion kWh of electricity each year. As more nuclear capacity is brought online, the coal burn will decrease and even with deferment of 8 units, the coal consumption will not get back to current levels until the late 1990s.

## NATIONAL LOAD GROWTH

The actual 1980 generating capacity by fuel type is shown in Figure 4. Data for the following analyses are primarily from 1981 Annual Report to

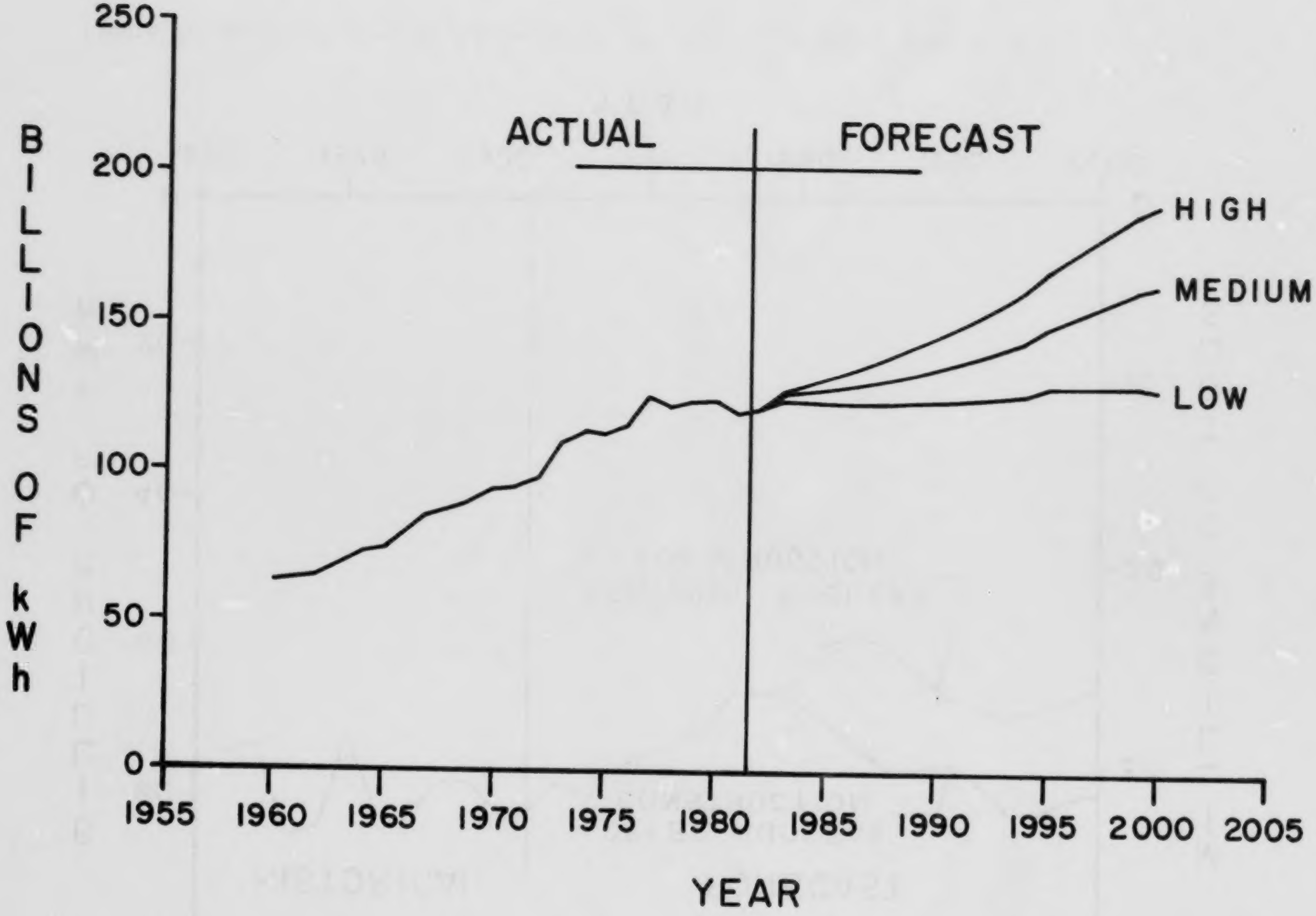


Figure 2. TVA energy requirements--historical growth and long-term outlook (billions of kWh)(Ref. 2).

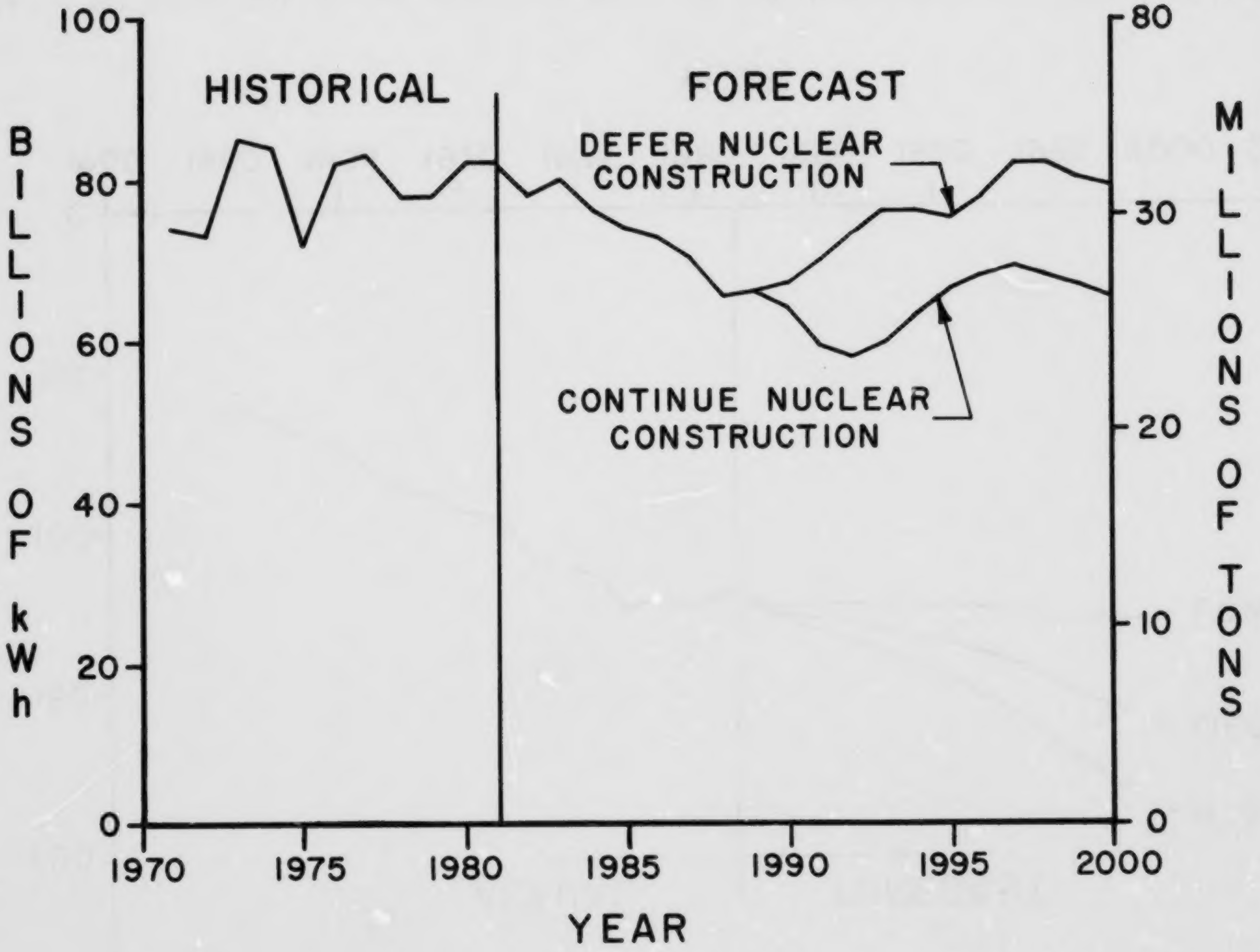


Figure 3. Expected level of operation of TVA coal-fired units (Ref. 2).

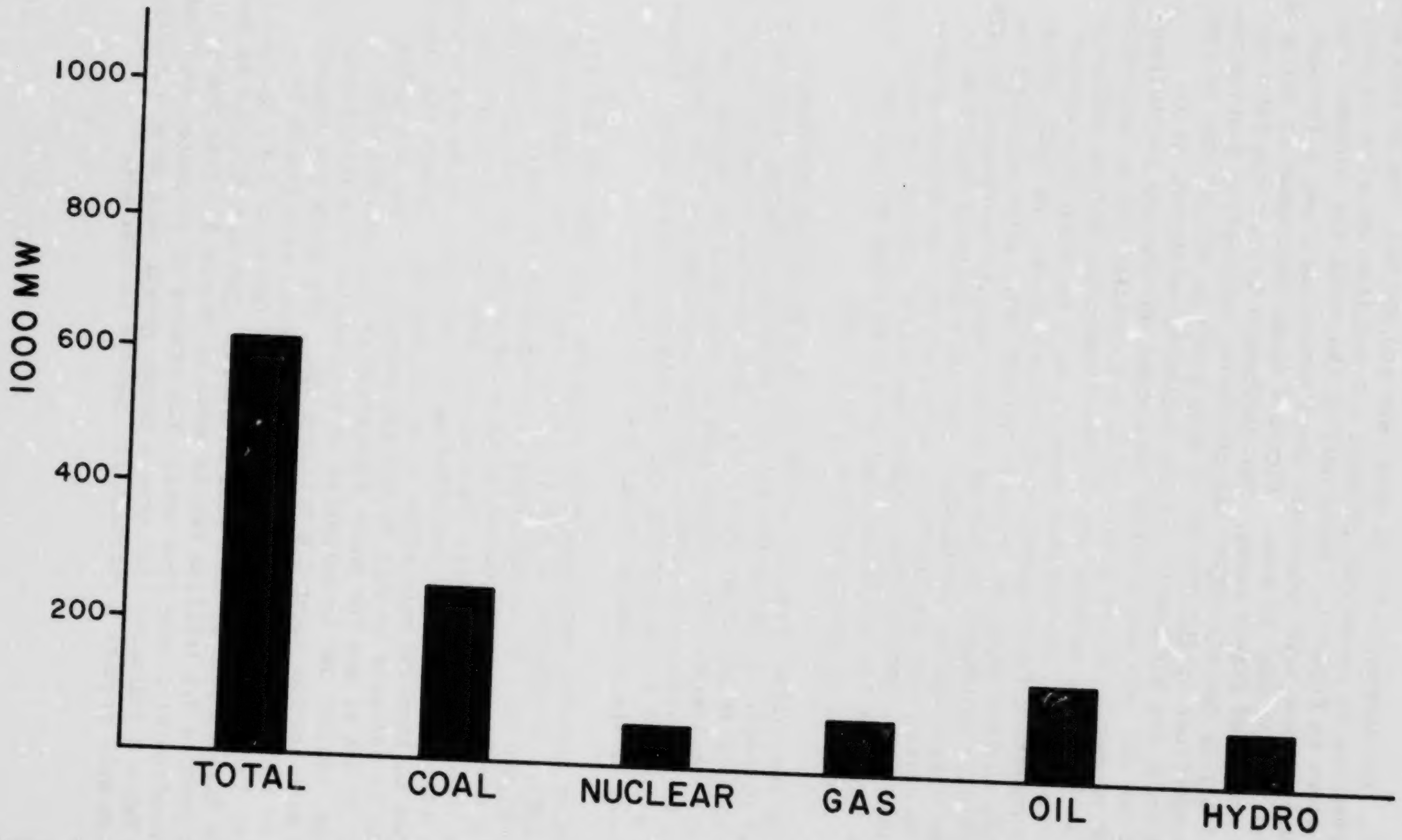


Figure 4. Actual 1980 electric generating capacity (Ref. 4).

Congress (3). The current total is just over 600,000 MW. Use of this mix of capacity resulted in production of about 2.2 trillion kWh with the fuel distribution shown in Figure 5. About half of the total was produced from coal. In order to make some judgements about future coal use, a forecast of energy requirements must be made. Figure 6 shows that there is not good agreement on projected growth rates. The difference between the National Electric Reliability Council (NERC) and the Energy Information Administration (EIA) projections of 250,000 GWh in 1985 grows to 400,000 GWh in 1990 or about 15% above the EIA level. In the following estimates, it is assumed that the EIA data are a better approximation although projections made in times of recession are likely to be understated just as projections made during an expanding economy led to overstatements. Before estimates of coal use can be made, the nuclear capacity must be taken into account because fuel economics favor operation of nuclear units. In 1980, 60,000 MW of existing nuclear capacity produced 260,000 GWh. After allowing for announced schedule slippages, 60,000 MW of new capacity is planned by 1985 (6). Further delays appear inevitable. Only an additional 20,000 MW is assumed to be operational and the total contribution from nuclear generation is assumed to be 390,000 GWh. Hydro and others account for about 300,000 GWh. To meet the projected load of 2.6 trillion kWh in 1985, 1.91 trillion will have to be generated from fossil fuel.

Existing coal-fired capacity totals 250,000 MW and an additional 70,000 MW is planned. Allowing for actual announced slippage, only 40,000 MW of new capacity is likely by 1985 (6). At an overall capacity factor of 0.5 based on peak demand, 640 million tons of coal will be needed. No new oil- or gas-fired capacity is assumed and the contribution from these sources is estimated at 290,000 GWh and 400,000 GWh respectively. Figure 7 shows that 64% of the estimated fossil fuel will be coal.

Estimates for 1995 were also made using the same approach but with less certainty. In addition to the projected 1985 nuclear capacity of 80,000 MW, 80,000 more is on the books for completion by 1995. Many of these units are likely to be cancelled or deferred beyond the mid-1990s and only those that are now at least 20% complete were included in the 1995 estimated total of 120,000 MW contributing 700,000 GWh. Hydro generation is projected to increase only slightly to 340,000 GWh. Generation from oil is expected to decrease to only 80,000 GWh because of renewed pricing pressure. If use of gas for power generation is not prohibited by regulations, 180,000 GWh is estimated to be produced from this source. Coal then must provide about 2.0 trillion kWh. The projected coal-fired capacity in 1985 plus completion of scheduled units will result in a capacity of 350,000 MW. At an average capacity factor of 0.6, approximately one billion tons of coal will be needed. The distribution by fuel source to produce 3.3 trillion kWh is shown in Figure 8. Over 60% of the total generation will come from coal. The summary of projected coal use shown in Table 2 indicates that even a modest growth rate in electricity consumption will require a substantial increase in coal use.

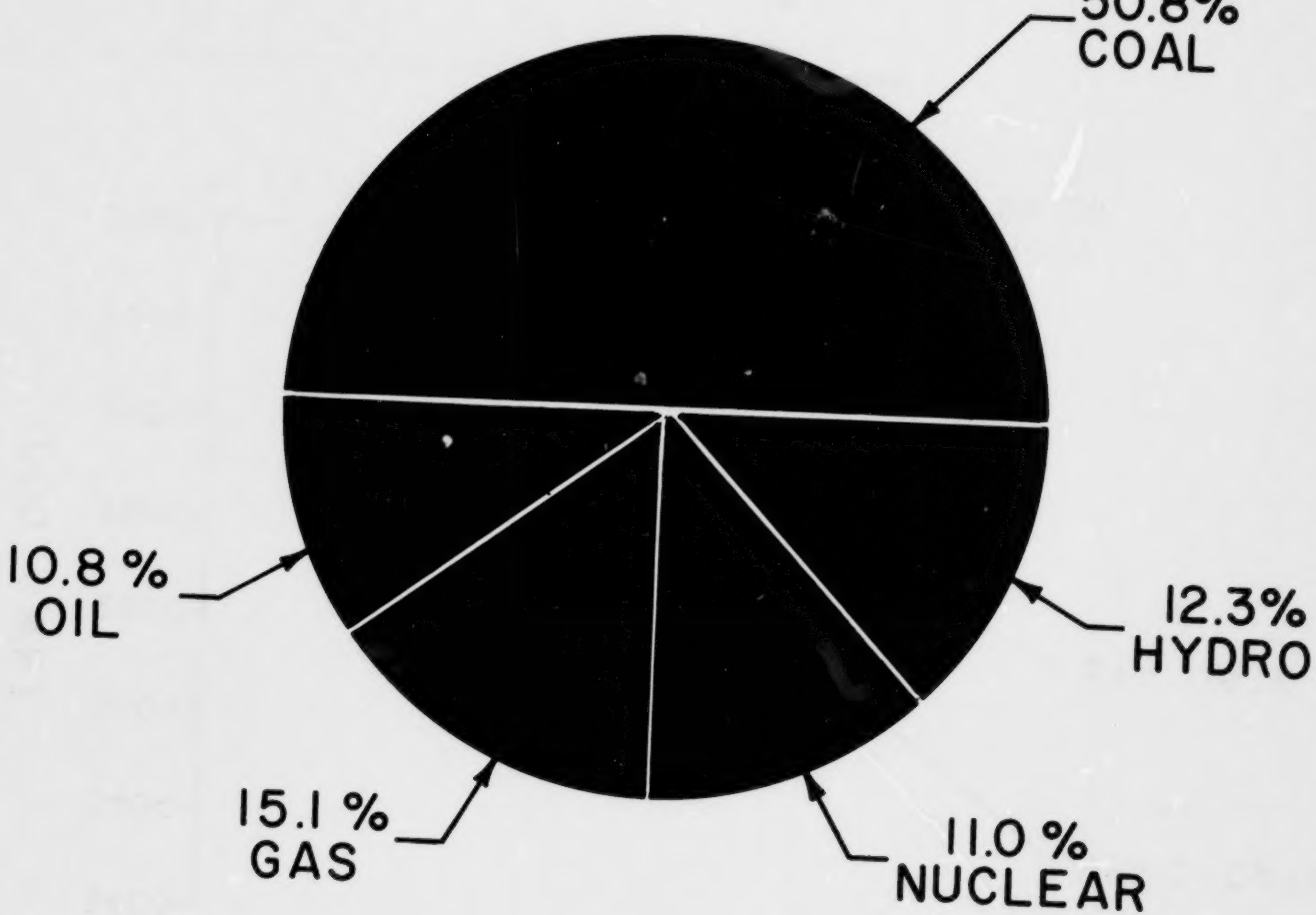


Figure 5. 1980 electricity generation (2.2 trillion kWh)(Ref. 3).

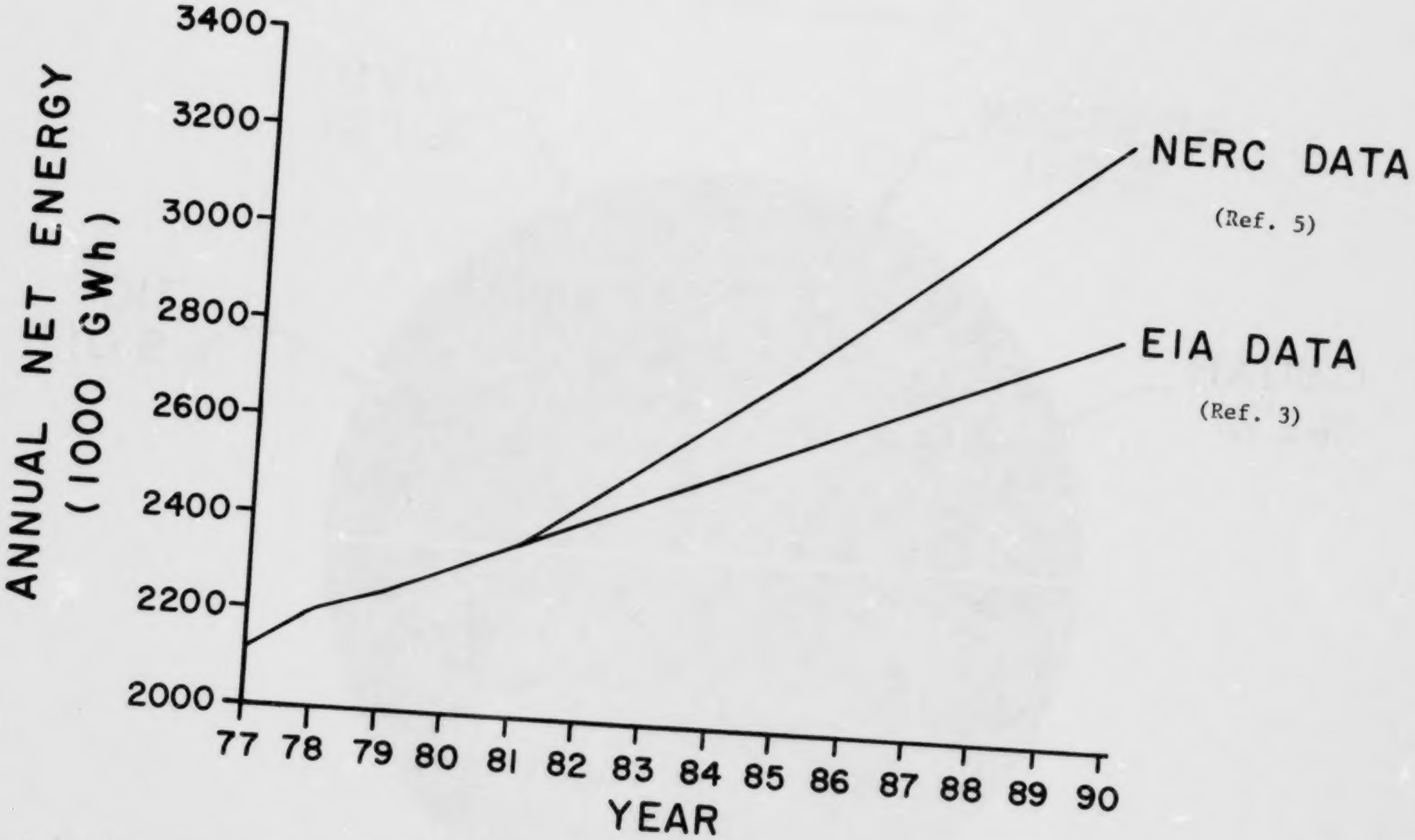


Figure 6. Net annual energy requirements--total contiguous United States.

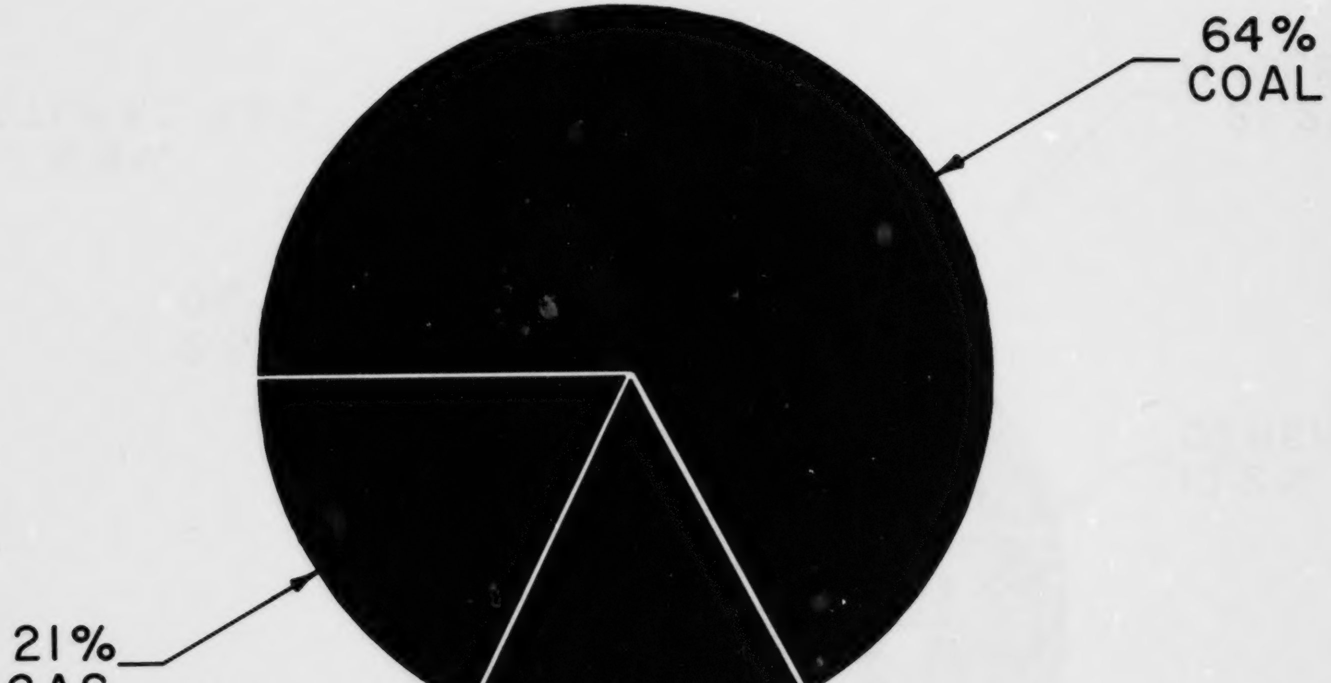


Figure 7. 1985 electricity generation from fossil fuel (1.91 trillion kWh).

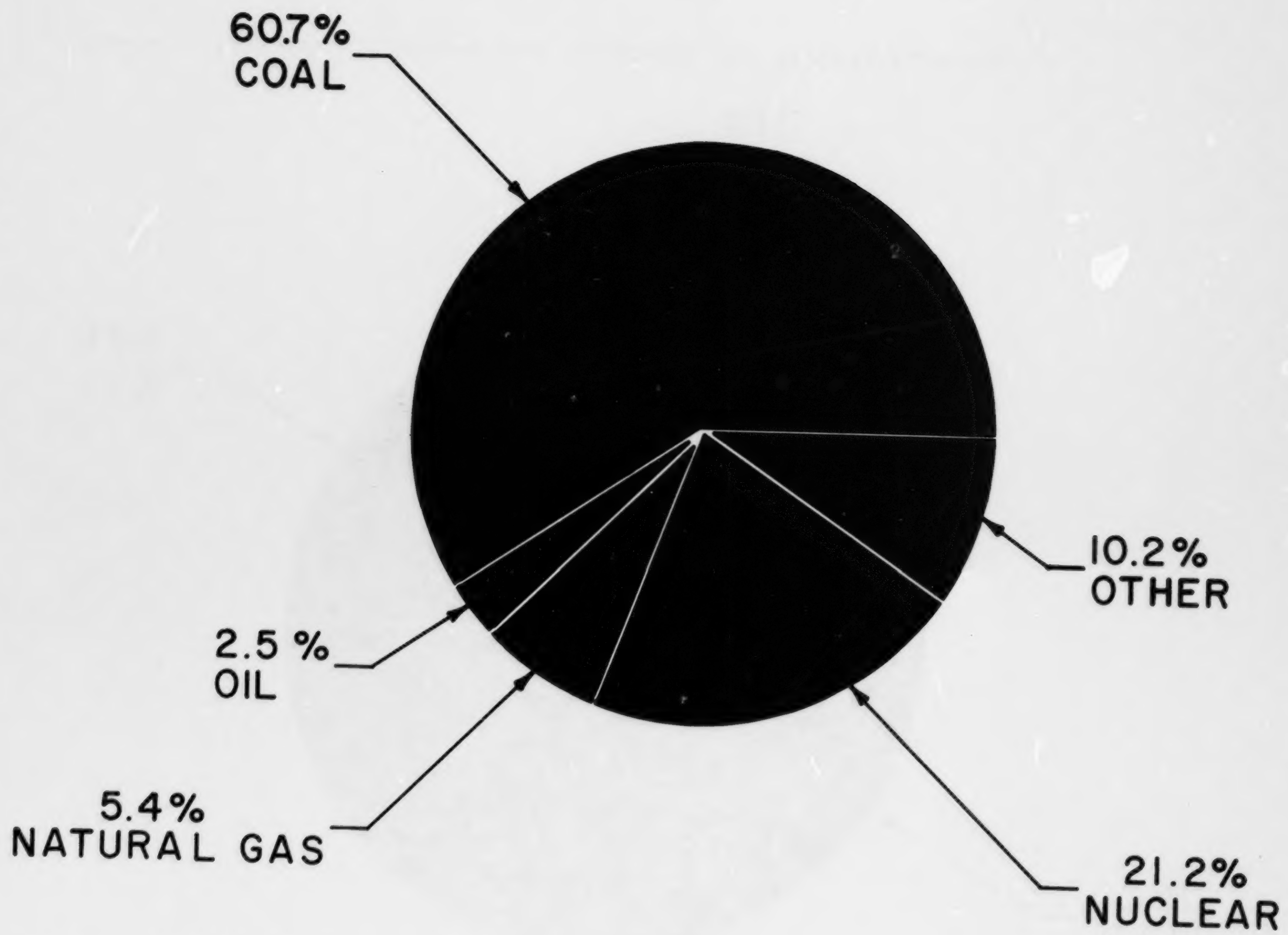


Figure 8. 1995 electricity generation (3.3 trillion kWh)(Ref. 3).

TABLE 2. COAL CONSUMPTION BY ELECTRIC UTILITIES

| Year | Million short tons |
|---|---|
| 1980 actual | 550 |
| 1985 estimate | 640 |
| 1995 estimate | 1000 |

The projections were made as if the whole industry were one giant system, which of course is a huge oversimplification. Each individual system will have to take into account generating mix and fuel availability and price. Trade-offs between coal and oil or gas are likely to occur. However, the estimated coal consumption is based on existing and actual planned capacity. The need for coal-fired generation will stretch the capability of the units. Performance and reliability will become more important than ever. EPRI program objectives include work to improve components of coal-fired systems not only for FGD units but power generation and distribution facilities as well.

## ALTERNATIVES TO FGD

A comprehensive treatment of FGD technology is covered in the papers presented at the symposium. Two alternatives to FGD that are covered by EPA and EPRI in other technical meetings are described here only as an introduction to the subjects.

Coal cleaning is a term that applies to a wide range of treatment methods to improve coal quality. Cleaning can be as simple as removing large rocks and tree stumps to chemical processes that remove organic sulfur. Improving coal quality has many advantages aside from removing sulfur to facilitate compliance and interest in the more sophisticated methods is growing. Some of the benefits and penalties of coal cleaning are shown below:

- Transportation costs
- Pension and benefit trust fund
- Pulverization costs
- Boiler capacity
- Boiler performance
- Ash Handling
- FGD operation
- FGD capital and operating costs
- ESP size and cost
- Surface moisture

All except the last two items are incentives to improve coal quality and TVA in a current study for EPA is attempting to quantify these factors. In this same study, the potential for use of coal cleaning in conjunction with FGD is being evaluated. Economic studies are based on use of the physical coal-cleaning method shown in Figure 9 and on a limestone scrubbing process

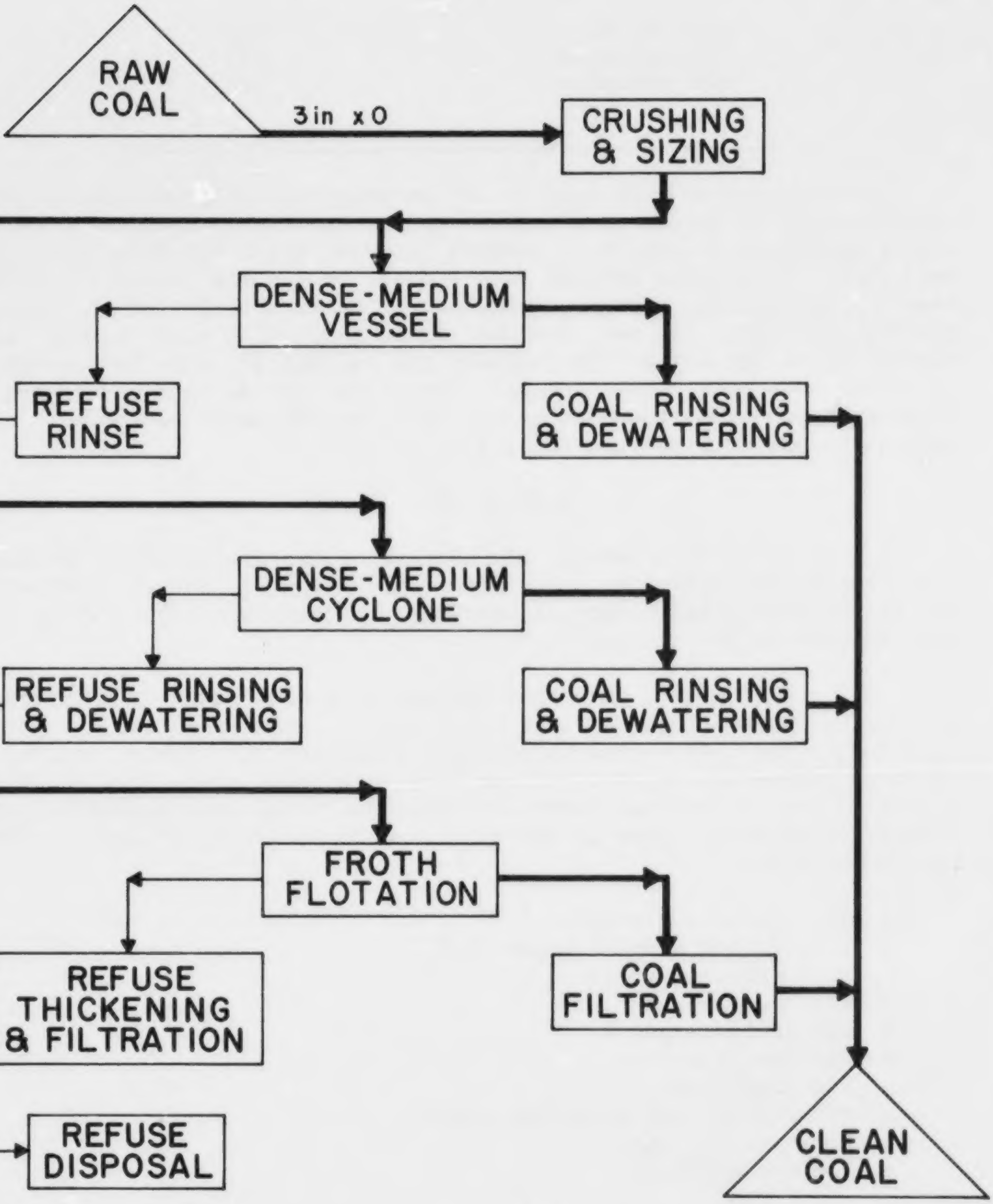


Figure 9. PCC process 1.

utilizing a spray tower and forced oxidation. The coal-cleaning process utilizes dense-medium separation and froth flotation for fines recovery. The results of one case studied are shown in Figure 10 for 1000-MW capacity. With 95% Btu recovery in the coal-cleaning plant and use of FGD to meet the 1979 new source performance standard (NSPS), combined coal cleaning and FGD are more economical (lower annual revenue requirements) than FGD alone if the coal sulfur content is above 4% and credit (benefits minus penalties) is taken for improved coal quality. With higher emission limits, the break-even point shifts toward lower sulfur coal; lower Btu recovery in the coal-cleaning process would have the opposite effect. Results of other cases together with the detailed premises and data will be available later this year when the coal-cleaning report is published.

An alternative method for combustion of coal to produce steam for power generation is advancing rapidly. The method involves burning coal in a fluidized bed at atmospheric pressure and is called atmospheric fluidized bed combustion (AFBC).

A major advantage of an AFBC boiler is the potential to burn coal in compliance with EPA sulfur dioxide emission limits without the need for a FGD system. The ability to capture sulfur dioxide in the combustion process eliminates the need of wet limestone scrubbers, which reduce the overall plant efficiency and increase the plant's cost. In addition, studies indicate that the dry, solid by-product of AFBC combustion, calcium sulfate, may have useful applications or may at least provide a material which can be disposed of economically. Furthermore, the combustion temperature is maintained below the ash softening temperature thus offering the potential for more cost-effective utilization of low-grade fuels than is possible with conventional boilers. Also, because of the reduced combustion temperature, the formation of nitrogen oxides, a pollutant which is receiving increasing attention, is greatly reduced. Another advantage of the AFBC process is the high heat transfer of the boiler tubes within the fluidized bed. This provides approximately twice the heat transfer coefficient of a conventional coal-fired boiler, reducing the physical size of the boiler. These advantages combine to result in a utility power plant that is potentially lower in capital and operating cost (approximately 10% to 15%) than a conventional pulverized coal plant with wet limestone scrubbers.

Results of experimental work sponsored by EPRI, EPA, DOE, utilities, and vendors have resulted in marked improvements in AFBC technology in the last few years. Particularly important developments are:

- For 90% sulfur removal, the amount of limestone required has been cut in half, to a Ca/S ratio of about 2.

- Nitrogen oxide emissions have been reduced by more than one half, and meet NSPS.

- Combustion efficiency has been increased to above 99%.

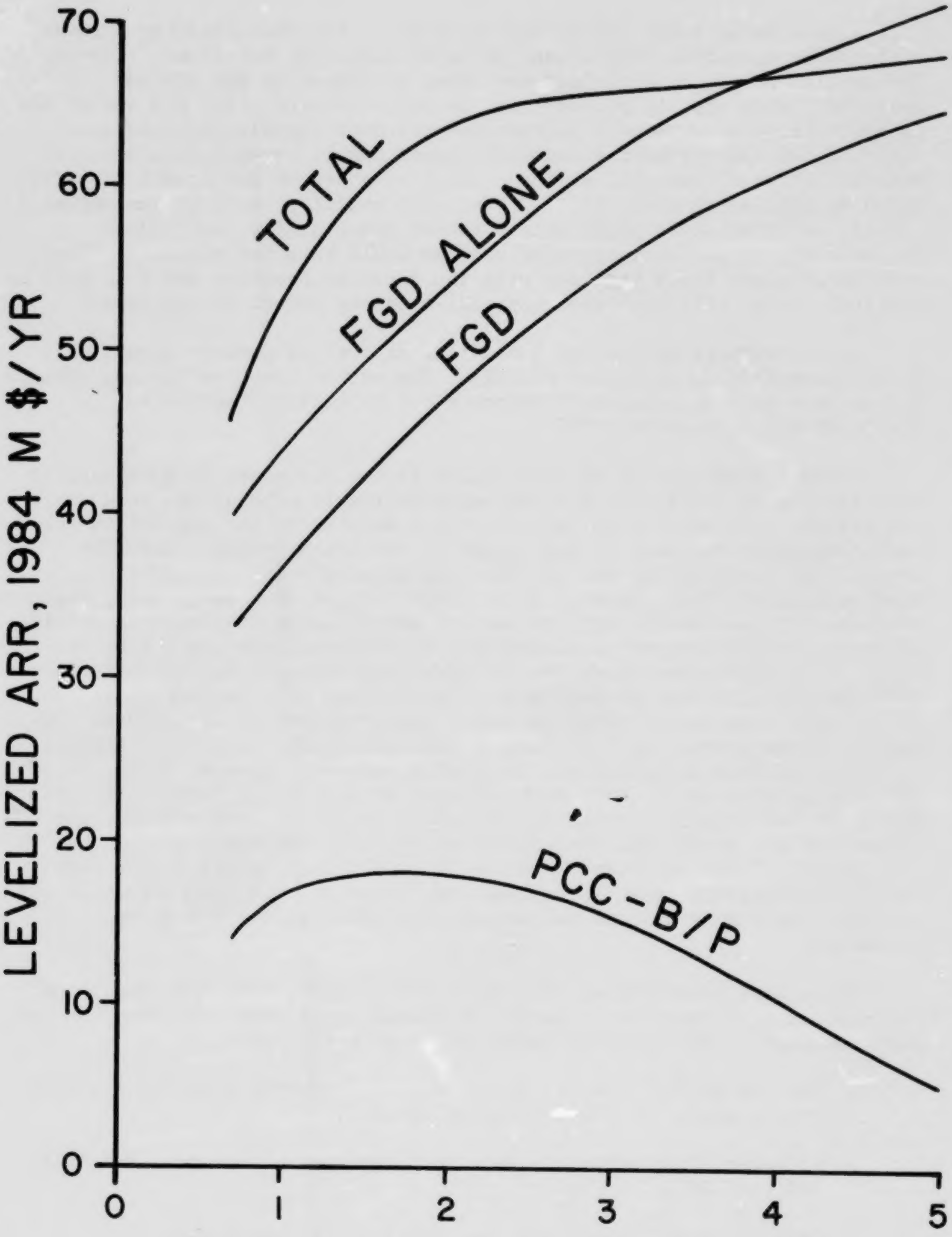


Figure 10. 95% Btu recovery; 79 NSPS.

In a cooperative program with EPRI, TVA has constructed and begun operation of a 20-MW AFBC pilot-plant boiler at the Shawnee Steam Plant. The test unit was designed by Babcock & Wilcox. A schematic drawing of the plant is shown in Figure 11. The test program is scheduled to extend through 1985 and results will be used in the design of a larger scale, 150- to 200-MW, prototype unit. In response to a request by EPRI, TVA along with several other utilities has offered to provide the site and share in the development of the prototype. The tentative schedule would lead to commercialization of the technology by the late 1990s.

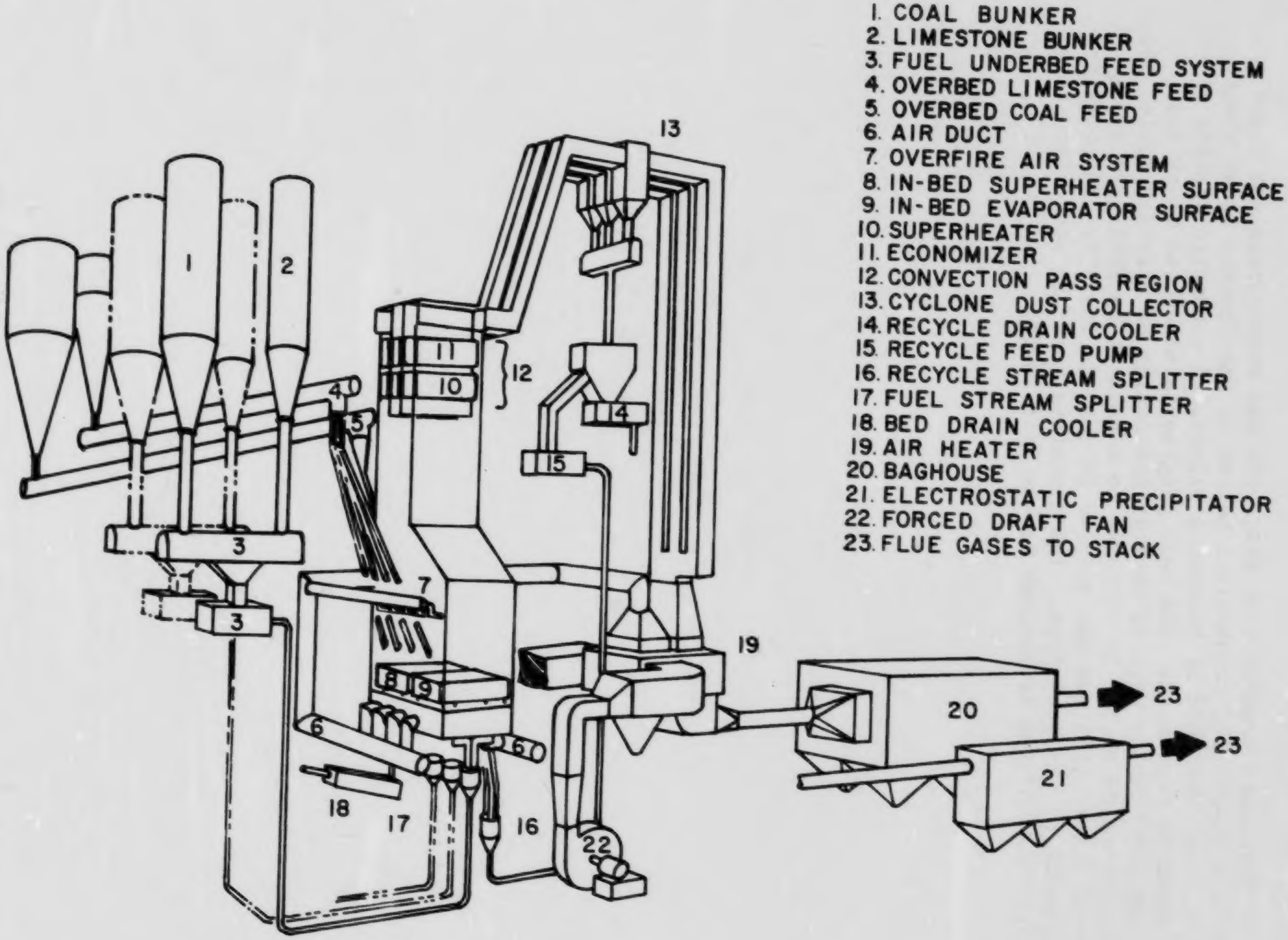


Figure 11. TVA 20-MW AFBC pilot plant--powerhouse arrangement.

## REFERENCES

1. From a composite graph prepared by the author in 1972 (unpublished).

2. Tennessee Valley Authority. "Review of the TVA Load Growth/Plant Construction Situation," January 1982.

3. U.S. Department of Energy, Energy Information Administration. 1981 Annual Report to Congress, Energy Projections, Vol. 3, DOE/EIA-0173(81)/3, February 1982.

4. U.S. Department of Energy, Energy Information Administration, Assistant Administrator for Energy Data Operations. Inventory of Power Plants in the United States 1980 Annual, DOE/EIA-0095(80), June 1981.

5. April Reliability Council Reports.

6. Technical Publishing. New Generating Plants, Power Engineering, April 1981.

## DISCLAIMER

This paper was prepared by the Tennessee Valley Authority (TVA). Neither TVA nor any person acting on its behalf:

a. makes any warranty or representation, express or implied, with respect to the use of any information contained in this paper, or that the use of any information, apparatus, method, or process disclosed in this paper may not infringe privately owned rights; or

b. assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this paper.

This paper does not necessarily reflect the views and policies of TVA.

## STATUS OF AIR QUALITY LEGISLATION/REGULATIONS

by: Walter C. Barber
Director, Office of Air Quality Planning
and Standards
U.S. Environmental Protection Agency, MD-10
Research Triangle Park, NC 27711

This was a verbal presentation; no abstract or paper was submitted.

## STATUS OF SOLID WASTE REGULATIONS

by: Stephen A. Lingle
Chief, Technology Branch
Hazardous and Industrial Waste Division
U.S. Environmental Protection Agency, WH-565
Washington, DC 20460

This was a verbal presentation; no abstract or paper was submitted.

# TRENDS IN COMMERCIAL APPLICATION OF FGD TECHNOLOGY

by: B. A. Laseke, Jr., M. T. Melia,
and N. G. Bruck
PEDCo Environmental, Inc.
Cincinnati, OH 45246

## ABSTRACT

PEDCo Environmental, Inc., under contract to the U.S. Environmental Protection Agency/Industrial Environmental Research Laboratory - Research Triangle Park, has been monitoring the status of utility flue gas desulfurization (FGD) since 1974. Information for this program is obtained by visits to plants having operational FGD systems and through periodic contacts with the owner/operator utilities, FGD system and equipment suppliers, design/engineering firms, research organizations, and regulatory agencies.

The information collected in this program is stored in the Flue Gas Desulfurization Information System (FGDIS), which is a collection of computerized data base files containing descriptive, design, performance, and cost data for all the FGD systems identified in FGDIS. FGDIS has the dual capability of generating the quarterly survey report as well as permitting immediate access to the data files via remote terminal access. This latter feature allows private and government users to access directly FGDIS at any time in order to conduct custom-designed data analyses, examine detailed data that are too specific to be conveniently included in the quarterly report, or review information that has been loaded into the system but not yet published in the quarterly report.

This paper summarizes the status of FGD technology as of January 1982 and highlights recent trends in process selection, design, costs, and performance of FGD systems. This discussion focuses on the logic and methodology used to store and retrieve this information in FGDIS. Particular attention is given to the structure diagram of FGDIS, individual data fields, and data access/manipulation procedures.

## NOTES

1. Company Names and Products.

   The mention of company names or products is not to be considered an endorsement or recommendation for use by the U.S. Environmental Protection Agency.

2. Consistency of Information.

   The information presented was obtained from a variety of sources including system vendors, users, EPA trip reports, and other technical reports. As such, consistency of information on a particular system and between the several systems discussed may be lacking. The information presented is basically that which was voluntarily submitted by developers and users with some interpretation by the author. The order of presentation of information or the amount of information presented for any one system should not be construed to favor or disfavor that particular system.

3. Units of Measure.

   EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice will result in undue cost of difficulty in clarity, IERL-RTP provides conversion factors for the non-metric units. Generally, this paper uses British units of measure.

   The following equivalents can be used for conversion to the Metric system:

| British | Metric |
|---|---|
| 5/9 (°F-32) | °C |
| 1 ft | 0.3048 m |
| 1 $ft^2$ | 0.0929 $m^2$ |
| 1 $ft^3$ | 0.0283 $m^3$ |
| 1 grain | 0.0648 gram |
| 1 lb (avoir.) | 0.4536 kg |
| 1 ton (long) | 1.0160 m tons |
| 1 ton (short) | 0.9072 m tons |
| 1 gal. | 3.7853 liters |
| 1 lb/$10^6$ Btu | 429.6 ng/J |
| 1 Btu/kWh | 1055.056 J/kWh |

# SECTION 1

# INTRODUCTION

For more than 8 years PEDCo Environmental, Inc., under contract to the U.S. Environmental Protection Agency (EPA), has monitored the development and growth of flue gas desulfurization (FGD) technology for fossil fuel-fired utility boilers in the United States. The program provides an objective and current perspective of FGD technology as applied to fossil fuel-fired utility boilers and facilitates, through information dissemination, improvements in the design and performance of current and future systems.

Utilities, system and equipment suppliers, system designers, research organizations, regulatory agencies, and others all volunteer the information for this program. This voluntary approach facilitates timely dissemination of pertinent information in this key technological area.

All information gathered for this program is loaded into a computerized database called the Flue Gas Desulfurization Information System (FGDIS). A description of the FGDIS is given in the following paragraphs.

Design and performance data for both the operational and planned domestic utility FGD systems are stored in FGDIS. Also stored are data on operational domestic scrubbers for removal of particulate matter and data on operational FGD systems applied to coal-fired utility boilers in Japan.

The design data contained in FGDIS encompass the entire emission control system and the power-generating unit to which it is applied. Descriptions include location, standards limiting emissions of $SO_2$ and particulate matter, power-generating capacity, boiler and stack information, average fuel analyses, and other more general data. Input of design data specific to FGD systems ranges from general information such as process type, system supplier, and initial system startup date to more specific component design information and operating parameters such as absorber type, gas and liquid flow rates, and pressure drop. Also included in the data are descriptions of the methods of solids concentrating and waste disposal, flue gas reheat, and mist elimination, and information on capital costs and annual revenue requirements of FGD systems.

For operational FGD systems, FGDIS stores comprehensive performance data, including periodic dependability parameters and the service times from which they are calculated. Where available, actual system $SO_2$ and particulate matter removal efficiencies are included (and qualified). Problems encountered with system operation and solutions implemented to correct them are described. The performance of the FGD-equipped boiler is described in terms of service time, production (kWh), and capacity factor.

Figure 1-1 presents a complete FGDIS structure diagram illustrating all of the information areas and some of the key data entries contained in the system, as well as the hierarchy associated with them in the data base. General unit data are at Level 0, whereas most of the specific component data are at Level 3.

In addition to being used to generate a quarterly report, FGDIS is also available for direct on-line access. This important function not only provides interested parties with an opportunity to examine data that are too specific for convenient inclusion in the quarterly report, but it also provides immediate access to information that has been loaded into the system but not yet published (i.e., information that has become available during the period between quarterly reports). Information is gathered, reduced, verified, and loaded into the FGDIS on a continual basis to ensure that the files remain current and complete.

Access to the FGDIS data files and manipulation of these data are accomplished via Intel Corporation's System 2000®. This comprehensive data base management system offers extensive data retrieval capabilities. The set of user-oriented commands provided are flexible enough to satisfy virtually any information need. The PRINT command will produce the compilation of a simple sequential list, or a set of report writer commands will produce a tabulation of the requested data in a predetermined report format. Utilization of system functions (average, standard deviation, summation, maximum value, minimum value) will elicit statistical analyses of the numerical data in the files. In addition, the data requested through the available commands can be selectively limited by a set of criteria included in the commands. This feature facilitates examination of design or performance parameters for a specific unit or a specific process type, and so on. The retrieval possibilities are limited only by the needs and imagination of the user.

The FGDIS files are stored at EPA's National Computer Center (NCC) in Research Triangle Park, North Carolina, and are accessible via a nationwide communications network consisting of local telephone numbers in 21 cities and WATS services.

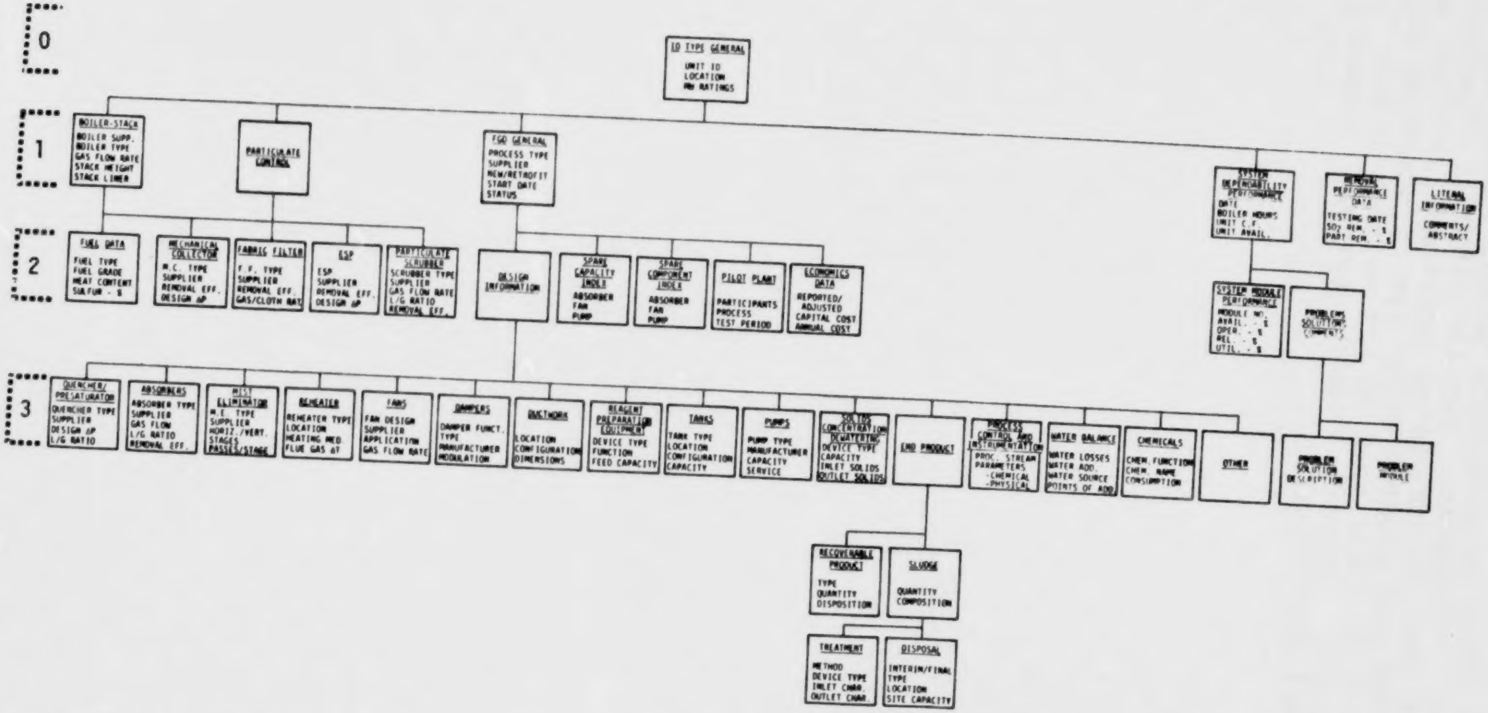


Figure 1-1. FGDIS structure diagram showing some key data fields.

Access to the FGDIS is available to the public through the National Technical Information Service (NTIS), Springfield, Virginia. In addition to providing continual on-line access capability, NTIS also can process selective information requests for limited information needs that do not warrant acquisition of a permanent computer account number (single requests for specific tabulated information).

# SECTION 2

# TECHNOLOGY OVERVIEW

## CURRENT STATUS

Table 2-1a lists the number of domestic utility FGD systems according to status and equivalent electrical capacities as of January 1982.

TABLE 2-1a. NUMBER AND TOTAL CAPACITY OF FGD SYSTEMS, JANUARY 1982

| Status | No. of units | Total controlled capacity, MW[a] | Equivalent scrubbed capacity, MW[b] |
|---|---|---|---|
| Operational | 94 | 35,931 | 32,683 |
| Under construction | 40 | 17,386 | 16,666 |
| Planned: | | | |
| Contract awarded | 17 | 10,035 | 9,819 |
| Letter of intent | 10 | 7,643 | 7,585 |
| Requesting/evaluating bids | 10 | 5,630 | 5,630 |
| Considering only FGD | 51 | 30,726 | 30,398 |
| TOTAL | 222 | 107,351 | 102,781 |

[a] Total controlled capacity (TCC) represents the gross capacities (MW) of coal-fired units brought into compliance by FGD systems, regardless of the percent of the flue gas treated.

[b] Equivalent scrubbed capacity (ESC) represents the effective capacities of the FGD systems (in equivalent MW), based on the percent of the flue gas treated. Unless otherwise noted, all capacities presented in the balance of this text are given in ESC.

Table 2-1a is generated by one of the "canned" programs in the FGDIS called TOTMW. The table is assembled as it appears automatically using one command. Table 2-1b shows the actual data fields that are accessed so that the table can be generated. All data items are pulled from Level 0 shown in the FGDIS structure diagram (Figure 1-1) except FGD current status which is accessed from FGD GENERAL in Level 1.

TABLE 2-1b. FGDIS FIELDS FOR GENERATION OF TABLE 2-1a.

FOREIGN - DOMESTIC
$SO_2$ & PARTICLE/PARTICLE
GROSS UNIT GENERATING CAPACITY - MW
EQUIVALENT SCRUBBED CAPACITY - MW
FGD CURRENT STATUS - 1/2/3/4/5/6/7/8

## GROWTH TRENDS

### Process Type

FGD systems may be categorized in several ways, some general and others more specific. Some general categorizations used in the survey are:

- wet or dry
- throwaway or salable product
- process (lime, limestone, dual alkali, etc.)

Tables 2-2a, 2-3a, and 2-4a summarize the current status of FGD capacities associated with each of the foregoing categories. Table 2-2a shows that the vast majority of the currently operating systems are wet processes. Dry systems represent greater than 6% of the FGD capacity for the operating and planned categories combined.

Table 2-3 indicates that approximately 5% of the current operating FGD-controlled capacity produces a salable product (elemental sulfur or sulfuric acid). Moreover, greater than 9% of the units currently under construction will produce a salable waste product.

Table 2-4a reflects the industry's strong preference for lime/limestone slurry FGD processes as they currently account for approximately 83% of the chemical processes selected.

### Emission Control Strategy

For FGD-equipped, coal-fired utility boilers, three basic combinations of primary particulate matter/$SO_2$ control strategies are used: electrostatic precipitator (ESP)/FGD, fabric filter (FF)/FGD, and two-stage scrubbing. Table 2-5a summarizes emission control strategies for the current and planned FGD-equipped units.

TABLE 2-2a. COMMITTED FGD CAPACITY - WET VS. DRY PROCESSES

| | FGD capacity, MW | | | |
|---|---|---|---|---|
| | Operational | Under construction | Contract awarded | Total |
| Wet | 36,690 | 14,878 | 7,646 | 59,214 |
| Dry | 550 | 2,538 | 1,019 | 4,107 |
| TOTAL | 37,240 | 17,416 | 8,665 | 63,321 |

Table 2-2b shows the FGDIS data fields accessed to prepare Table 2-2a. Data from the first three fields is drawn from Level 0 on Figure 1-1. The last two fields are accessed from FGD GENERAL in Level 1.

TABLE 2-2b. FGDIS FIELDS FOR GENERATION OF TABLE 2-2a.

FOREIGN - DOMESTIC
$SO_2$ & PARTICLE/PARTICLE
EQUIVALENT SCRUBBED CAPACITY - MW
$SO_2$ REMOVAL MODE - WET SCRUBBING/SPRAY DRYING
FGD CURRENT STATUS - 1/2/3/4/5/6/7/8

TABLE 2-3a. DISTRIBUTION OF FGD SYSTEMS BY END-PRODUCT

| | FGD capacity, MW | | | |
|---|---|---|---|---|
| | Operational | Under construction | Planned | Total |
| Salable product | 1,600 | 1,589 | 475 | 3,664 |
| Throwaway product | 31,083 | 15,077 | 27,680 | 73,840 |
| TOTAL | 32,683 | 16,666 | 28,155 | 77,504 |

Table 2-3a was prepared by accessing the FGDIS data fields shown in Table 2-3b. Data from the first three fields are drawn from Level 0 in Figure 1-1. The other fields are found in Level 1 under the FGD GENERAL DATA "tree".

TABLE 2-3b. FGDIS FIELDS FOR GENERATION OF TABLE 2-3a.

FOREIGN - DOMESTIC
$SO_2$ & PARTICLE/PARTICLE
EQUIVALENT SCRUBBED CAPACITY - MW
SALABLE PRODUCT/THROWAWAY PRODUCT
FGD CURRENT STATUS - 1/2/3/4/5/6/7/8

TABLE 2-4a. DISTRIBUTION OF FGD SYSTEMS BY PROCESS

| Process | FGD capacity, MW | | | |
|---|---|---|---|---|
| | Operational | Under construction | Planned | Total |
| Limestone[a] | 15,578 | 8,179 | 14,085 | 37,842 |
| Lime[b] | 12,499 | 4,270 | 4,940 | 21,709 |
| Lime/spray drying | 110 | 2,338 | 1,019 | 3,467 |
| Lime/limestone | 20 | 0 | 475 | 495 |
| Lime/sodium carbonate | 0 | 100 | 0 | 100 |
| Sodium carbonate | 1,255 | 0 | 1,900 | 3,155 |
| Sodium carbonate/ spray drying | 440 | 0 | 0 | 440 |
| Magnesium oxide | 0 | 724 | 0 | 724 |
| Wellman-Lord | 1,540 | 534 | 0 | 2,074 |
| Dual alkali | 1,181 | 421 | 421 | 2,023 |
| Aqueous carbonate/ spray drying | 0 | 100 | 0 | 100 |
| Citrate | 60 | 0 | 0 | 60 |
| TOTAL | 32,683 | 16,666 | 22,840[c] | 72,189 |

[a] Includes alkaline fly ash/limestone and limestone slurry systems.
[b] Includes alkaline fly ash/lime and lime slurry systems.
[c] Because the processes of all planned systems are not yet selected, the totals in this status category are less than those in Table 2-1a.

Table 2-4b shows the FGDIS data fields used to assemble Table 2-4a. Data from the first three fields is drawn from Level 0 on Figure 1-1. PROCESS TYPE and CURRENT STATUS are accessed through FGD GENERAL in Level 1.

TABLE 2-4b. FGDIS FIELDS FOR GENERATION OF TABLE 2-4b.

FOREIGN - DOMESTIC
$SO_2$ & PARTICLE/PARTICLE
EQUIVALENT SCRUBBED CAPACITY - MW
PROCESS TYPE - LIME/LIMESTONE/ETC.
FGD CURRENT STATUS - 1/2/3/4/5/6/7/8

TABLE 2-5a. SUMMARY OF EMISSION CONTROL SELECTION

| | Operational | | Under construction | | Contract awarded | | Total | |
|---|---|---|---|---|---|---|---|---|
| | No. | MW | No. | MW | No. | MW | No. | MW |
| ESP/FGD | 62 | 21,989 | 26 | 11,315 | 14 | 8,170 | 102 | 41,474 |
| FF/FGD | 2 | 550 | 11 | 3,703 | 3 | 1,109 | 16 | 5,362 |
| Two-stage scrubbing | 27 | 10,144 | 3 | 1,648 | 0 | 0 | 33 | 11,792 |
| TOTAL | 94 | 32,683 | 40 | 16,666 | 17 | 9,189 | 152 | 58,538 |

Table 2-5b shows the FGDIS data fields used to generate Table 2-5a. The first three fields are in Level 0 of Figure 1-1. FGD CURRENT STATUS is in Level 1 under FGD GENERAL DATA. The last three fields are in Level 2 in the PARTICULATE MATTER CONTROL "tree".

TABLE 2-5b. FGDIS FIELDS FOR GENERATION OF TABLE 2-5a.

FOREIGN - DOMESTIC
$SO_2$ & PARTICLE/PARTICLE
EQUIVALENT SCRUBBED CAPACITY - MW
FGD CURRENT STATUS - 1/2/3/4/5/6/7/8
PART SCRUBBER GENERIC TYPE
FABRIC FILTER TYPE
ESP TYPE - HOT SIDE/COLDSIDE

Table 2-5a reflects several industry preferences with respect to selection of a control strategy. The most obvious is the strong preference to use an ESP for primary particulate matter control upstream of the FGD system. Second, a small but increasing preference for FF's is influenced by the advent of the spray dryer/dry collection FGD technology. The suppliers of most of the dry processes offered commercially recommend a FF as the preferred collection device. Third, a preference for the use of two-stage scrubbing for $SO_2$ and particulate matter control is diminishing. These planned systems will be used in those situations where the alkalinity of the collected flyash is used as a process additive.

Design $SO_2$ Removal, Coal Sulfur Content, and Inlet $SO_2$ Level

Table 2-6a presents a breakdown of the FGD systems that are operational, under construction, and planned (contract awarded) according to level of $SO_2$ removal efficiency versus coal sulfur content. Table 2-6a indicates that approximately 70% of the FGD capacity is designed for $SO_2$ removal efficiencies of 80% or greater. Moreover, approximately half of the total FGD capacity is for low-sulfur coal.

## TABLE 2-6a. DESIGN $SO_2$ REMOVAL EFFICIENCIES OF FGD SYSTEMS WITH RESPECT TO COAL SULFUR CONTENT

| Design removal efficiency | Coal sulfur content[a] | Operational | | Under construction | | Contract awarded | | Total | |
|---|---|---|---|---|---|---|---|---|---|
| | | No. | MW | No. | MW | No. | MW | No. | MW |
| < 70 | Low | 15 | 5,364 | 1 | 440 | 0 | 0 | 16 | 5,804 |
| | Medium | 5 | 746 | 0 | 0 | 0 | 0 | 5 | 746 |
| | High | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Total | | 20 | 6,110 | 1 | 440 | 0 | 0 | 21 | 6,550 |
| 70-79 | Low | 9 | 3,124 | 4 | 1,215 | 5 | 2,990 | 18 | 7,329 |
| | Medium | 4 | 1,362 | 0 | 0 | 0 | 0 | 4 | 1,362 |
| | High | 2 | 1,000 | 0 | 0 | 0 | 0 | 2 | 1,000 |
| Total | | 15 | 5,486 | 4 | 1,215 | 5 | 2,990 | 24 | 9,691 |
| 80-89 | Low | 10 | 3,085 | 5 | 2,874 | 2 | 999 | 17 | 6,958 |
| | Medium | 6 | 2,483 | 6 | 2,049 | 2 | 1,120 | 14 | 5,652 |
| | High | 12 | 4,443 | 3 | 1,675 | 0 | 0 | 15 | 6,118 |
| Total | | 28 | 10,011 | 14 | 6,598 | 4 | 2,119 | 46 | 18,728 |
| ≥ 90 | Low | 9 | 3,311 | 6 | 3,144 | 0 | 0 | 15 | 6,455 |
| | Medium | 13 | 5,431 | 5 | 1,079 | 3 | 1,975 | 21 | 8,485 |
| | High | 9 | 1,704 | 6 | 3,106 | 1 | 421 | 16 | 5,231 |
| Total | | 31 | 10,446 | 17 | 7,329 | 4 | 2,396 | 52 | 20,171 |
| TOTAL | Low | 43 | 14,884 | 16 | 7,673 | 7 | 3,989 | 66 | 26,546 |
| | Medium | 28 | 10,022 | 11 | 3,128 | 5 | 3,095 | 44 | 16,245 |
| | High | 23 | 7,147 | 9 | 4,781 | 1 | 421 | 33 | 12,349 |

[a] Low-sulfur content is less than 1%; medium-sulfur content is 1 to 3% sulfur; high-sulfur content is greater than 3%.

Table 2-6a is generated by drawing from the FGDIS data fields shown in Table 2-6b. The first three data fields are found in Level 0 of the database structure (Figure 1-1). The average sulfur content of the coal comes from Level 2 in the BOILER-STACK "tree". The last two fields (status and $SO_2$ removal efficiency) are found in Level 1 under FGD GENERAL DATA.

## TABLE 2-6b. FGDIS FIELDS FOR GENERATION OF TABLE 2-6a.

FOREIGN - DOMESTIC
$SO_2$ & PARTICLE/PARTICLE
EQUIVALENT SCRUBBED CAPACITY - MW
AVERAGE SULFUR CONTENT
FGD CURRENT STATUS - 1/2/3/4/5/6/7/8
TOTAL UNIT $SO_2$ DESIGN REMOVAL EFFICIENCY - %

# SECTION 3

# PROCESS DESIGN DEVELOPMENTS

This section highlights some of the major process design developments that have become evident in commercial FGD system technology.

## CHEMICAL ADDITIVES

Chemical additives are used to improve the chemistry of lime- and limestone-based FGD systems. The primary additive used to date has been magnesium; however, a number of others have been tested and used to some extent, the most prominent of which are adipic acid and sodium thiosulfate.

Table 3-1 lists the number and generating capacity of units that now have or will have FGD systems with additive-promoted processes.

TABLE 3-1a. NUMBER AND CAPACITY OF UNITS USING ADDITIVE-PROMOTED FGD PROCESSES

| Process | Operational | | Under construction | | Contract awarded | |
|---|---|---|---|---|---|---|
| | No. | MW | No. | MW | No. | MW |
| Lime | 12 | 6,961 | 0 | 0 | 0 | 0 |
| Limestone | 1 | 194 | 3 | 1,375 | 2 | 1,500 |
| TOTAL | 13 | 7,155 | 3 | 1,375 | 2 | 1,500 |

Table 3-1a was prepared by accessing the FGDIS data fields shown in Table 3-1b. Data from the first three data fields are drawn from Level 0 in Figure 1-1. The rest of the fields are found in Level 1 under the FGD GENERAL DATA "tree".

TABLE 3-1b. FGDIS FIELDS FOR GENERATION OF TABLE 3-1a.

FOREIGN - DOMESTIC
$SO_2$ & PARTICLE/PARTICLE
EQUIVALENT SCRUBBED CAPACITY - MW
PROCESS TYPE - LIME/LIMESTONE/ETC.
PROCESS ADDITIVES - MG/ADIPIC ACID/ETC.
FGD CURRENT STATUS - 1/2/3/4/5/6/7/8

## SYSTEM ENERGY CONSUMPTION

Table 3-2a shows the range and average of energy requirements of the more prominent FGD processes as a percentage of gross generating capacity for new and retrofit systems. As shown in the table, there is no significant difference between new and retrofit systems.

TABLE 3-2a. ENERGY CONSUMPTION FOR OPERATIONAL FGD SYSTEMS[a,b]

| Process | New | | Retrofit | |
|---|---|---|---|---|
| | Range | Average | Range | Average |
| Dual alkali | 0.8 - 2.4 | 1.6 | 1.0 | 1.0 |
| Lime | 1.2 - 6.0 | 3.4 | 1.0 - 3.5 | 2.0 |
| Limestone | 1.1 - 5.5 | 3.0 | 1.0 - 5.6 | 3.5 |
| Sodium carbonate | 0.2 | 0.2 | 0.2 - 1.5 | 0.5 |
| Wellman-Lord | 3.6 | 3.6 | 4.4 - 12.1 | 7.0 |

[a] Excluding flue gas reheat.

[b] Electrical energy consumption of the FGD installation as a percentage of gross unit generating capacity.

Table 3-2b shows the FGDIS data fields used to prepare Table 3-2a. The first five data fields can be found in Level 0 on the structure diagram shown in Figure 1-1 under the GENERAL DATA heading. The other two fields are located at the top of the FGD GENERAL DATA "tree" in Level 1.

TABLE 3-2b. FGDIS FIELDS FOR GENERATION OF TABLE 3-2a.

FOREIGN - DOMESTIC
$SO_2$ & PARTICLE/PARTICLE
GROSS UNIT GENERATING CAPACITY - MW
NET UNIT GENERATING CAPACITY WITH FGD - MW
NET UNIT GENERATING CAPACITY W/O FGD - MW
PROCESS TYPE - LIME/LIMESTONE/ETC.
NEW/RETROFIT

## COAL CHLORIDE CONTENT

Table 3-3a shows the breakdown of FGD systems according to the coal chloride content (where known) and status. The table shows that most FGD systems operate or will operate on flue gas generated by the combustion of low chloride coal. However, there are a significant number of units operating or planned to operate on high-chloride coal.

TABLE 3-3a. FGD SYSTEM COAL CHLORIDE CONTENTS

| Chloride content | Operational | | Under construction | | Contract awarded | |
|---|---|---|---|---|---|---|
| | No. | MW | No. | MW | No. | MW |
| <0.05% | 35 | 13,375 | 8 | 3,293 | 5 | 2,920 |
| 0.05-0.10 | 14 | 3,477 | 7 | 4,394 | 0 | 0 |
| 0.11-0.15 | 1 | 185 | 1 | 500 | 1 | 500 |
| 0.16-0.20 | 4 | 1,568 | 1 | 441 | 0 | 0 |
| >0.20 | 1 | 194 | 2 | 720 | 1 | 620 |

Table 3-3b lists the FGDIS data fields that were used to assemble Table 3-3a. The first three are in Level 0 on Figure 1-1. The last two are in Level 1 in the FGD GENERAL DATA "tree".

TABLE 3-3b. FGDIS FIELDS FOR PREPARATION OF TABLE 3-3a.

FOREIGN - DOMESTIC
$SO_2$ & PARTICLE/PARTICLE
EQUIVALENT SCRUBBED CAPACITY - MW
AVERAGE CHLORIDE CONTENT - %
FGD CURRENT STATUS - 1/2/3/4/5/6/7/8

## SLUDGE DISPOSAL

Table 3-4 is a breakdown of FGD systems according to sludge processing type, transportation, disposal method, site, and operational status. Information on units under construction and on which contracts are awarded is incomplete because final disposal strategies are often not finalized until plant construction is nearly complete.

TABLE 3-4a. NUMBER AND CAPACITY OF FGD SYSTEMS ACCORDING TO SLUDGE DISPOSAL METHOD AND STATUS

| Disposal Method | Operational |  | Under Construction |  |
|---|---|---|---|---|
|  | No. | MW | No. | MW |
| Sludge Processing Type |  |  |  |  |
| Untreated |  |  |  |  |
| Bleed to pond | 16 | 4,382 | 0 | 0 |
| Thickened | 5 | 1,530 | 0 | 0 |
| Dewatered | 4 | 470 | 3 | 1,501 |
| Treated |  |  |  |  |
| Forced oxidation | 12 | 5,958 | 6 | 3,415 |
| Fixation | 24 | 11,108 | 7 | 3,004 |
| Stabilization | 16 | 5,986 | 4 | 1,792 |
| Sludge Transportation |  |  |  |  |
| Conveyor | 2 | 1,140 | 0 | 0 |
| Pipeline | 8 | 3,486 | 1 | 495 |
| Rail | 3 | 1,785 | 1 | 500 |
| Truck | 23 | 6,865 | 9 | 3,569 |
| Pumped | 20 | 8,603 | 2 | 822 |
| Sludge Disposal Method |  |  |  |  |
| Landfill | 37 | 13,807 | 21 | 8,356 |
| Pond | 48 | 16,675 | 6 | 2,832 |
| Disposal Site |  |  |  |  |
| Onsite | 56 | 19,458 | 12 | 5,499 |
| Offsite | 15 | 6,983 | 3 | 560 |

Table 3-4b is a listing of the FGDIS data fields accessed for the preparation of Table 3-5a. The top three fields are located in Level 0 of Figure 1-1. The FGD CURRENT STATUS field appears in Level 1 under FGD GENERAL DATA. The other data fields are found at the bottom of this same "tree" under END PRODUCT.

TABLE 3-4b. FGDIS FIELDS FOR PREPARATION OF TABLE 3-4a.

FOREIGN - DOMESTIC
$SO_2$ & PARTICLE/PARTICLE
EQUIVALENT SCRUBBED CAPACITY - MW
FGD CURRENT STATUS - 1/2/3/4/5/6/7/8
TREATMENT METHOD
DISPOSAL SITE TRANSPORTATION METHOD - PIPELINE/TRUCK/ETC.
DISPOSAL LOCATION - ON-SITE/OFF-SITE
DISPOSAL GENERIC TYPE - LANDFILL/POND/ETC.
DISPOSAL SPECIFIC TYPE - DIKED/SIDE HILL/ETC.

# SECTION 4

# PERFORMANCE TRENDS

## OPERATING EXPERIENCE

In the several years, FGD has become the most commercially developed means of control of $SO_2$ emissions from coal-fired boilers. FGD operating experience increases each year as more and more systems are placed in service. The FGD survey program has been monitoring the performance of the operating FGD systems and logging monthly operating parameters (e.g., boiler and FGD system operating hours, forced outage times and scheduled outage times). With this operational information, system performance trends over the years can be graphed and analyzed.

## DEPENDABILITY

FGD system availability is defined as the hours the FGD is available for operation (whether operated or not) divided by hours in the period. Period hours are always equal to hours in a month. System availability is one of four parameters which characterize system dependability, the other three being operability, reliability, and utilization. This discussion, however, will be limited to system availability. Table 4-1a lists the four system parameters for 1981 for typical low sulfur (<1%), medium sulfur (1-3%), high sulfur (>3%) coal operations, respectively.

Table 4-1b shows the FGDIS data fields used to generate the information shown in Table 4-1a. Like Table 2-1a, the tables under the 4-1a heading are generated by a "canned" FGDIS program called PERAVG. These tables can be generated for any units for any given periods, etc. The data fields used in this program are listed in Table 4-1b. The first nine data fields are located in Level 0 under GENERAL DATA as shown in the structure diagram (Figure 1-1). All of the other fields are found under the UNIT PERFORMANCE "tree" in Levels 1 and 2.

# TABLE 4-1a. FGD DEPENDABILITY FIGURES FOR 1981 FOR A TYPICAL LOW-, MEDIUM-, AND HIGH-SULFUR COAL APPLICATION

NORTHERN STATES POWER
SHERBURNE
2

NET GENERATING CAPACITY WITH FGD = 700
GROSS GENERATING CAPACITY = 740
% SCRUBBED = 100

| DATE | CAPACITY FACTOR | PERIOD HOURS | BOILER HOURS | FGD HOURS | AVAILABILITY | OPERABILITY | RELIABILITY | UTILIZATION |
|---|---|---|---|---|---|---|---|---|
| 8101 | 76.5 | 744 | 744 | 744 | 100.0 | 100.0 | 100.0 | 100.0 |
| 8102 | 77.0 | 672 | 664 | 664 | 100.0 | 100.0 | 100.0 | 98.8 |
| 8103 | 78.8 | 744 | 744 | 744 | 100.0 | 100.0 | 100.0 | 100.0 |
| 8104 | 61.0 | 720 | 579 | 579 | 100.0 | 100.0 | 100.0 | 80.0 |
| 8105 | 69.0 | 744 | 679 | 679 | 100.0 | 100.0 | 100.0 | 91.0 |
| 8106 | 73.0 | 720 | 713 | 713 | 100.0 | 100.0 | 100.0 | 99.0 |
| 8107 | 72.0 | 744 | 741 | 741 | 100.0 | 100.0 | 100.0 | 99.0 |
| 8108 | 70.0 | 744 | 744 | 744 | 100.0 | 100.0 | 100.0 | 100.0 |
| 8109 | 58.0 | 720 | 616 | 616 | 100.0 | 100.0 | 100.0 | 85.0 |
| 8110 | 79.0 | 744 | 744 | 744 | 100.0 | 100.0 | 100.0 | 100.0 |
| 8111 | 73.0 | 720 | 720 | 720 | 100.0 | 100.0 | 100.0 | 100.0 |
| 8112 | 79.0 | 744 | 744 | 744 | 100.0 | 100.0 | 100.0 | 100.0 |
| AVERAGE | 72.2 | | | | 100.0 | 100.0 | 100.0 | 96.1 |

SOUTH MISSISSIPPI ELEC PWR
R.D. MORROW, SR.
2

NET GENERATING CAPACITY WITH FGD = 180
GROSS GENERATING CAPACITY = 200
% SCRUBBED = 62

| DATE | CAPACITY FACTOR | PERIOD HOURS | BOILER HOURS | FGD HOURS | AVAILABILITY | OPERABILITY | RELIABILITY | UTILIZATION |
|---|---|---|---|---|---|---|---|---|
| 8101 | 86.5 | 744 | 665 | 649 | 89.4 | 97.6 | 97.6 | 87.2 |
| 8102 | 74.9 | 672 | 576 | 575 | 100.0 | 99.9 | 100.0 | 85.6 |
| 8103 | 49.5 | 744 | 502 | 434 | 85.5 | 86.6 | 86.6 | 58.4 |
| 8104 | 71.5 | 720 | 640 | 627 | 99.5 | 98.0 | 99.[illegible] | 87.1 |
| 8105 | 77.4 | 744 | 699 | 693 | 100.0 | 99.1 | 100.0 | 93.1 |
| 8106 | 99.7 | 720 | 718 | 699 | 97.8 | 97.3 | 97.3 | 97.0 |
| 8107 | 80.9 | 744 | 716 | 695 | 100.0 | 97.1 | 99.6 | 93.4 |
| 8108 | 82.1 | 744 | 718 | 717 | 100.0 | 99.9 | 100.0 | 96.4 |
| 8109 | 75.4 | 720 | 720 | 706 | 98.1 | 98.1 | 98.1 | 98.1 |
| 8110 | 67.5 | 744 | 744 | 743 | 99.9 | 99.9 | 99.9 | 99.9 |
| 8111 | 19.1 | 720 | 236 | 233 | 32.4 | 98.8 | 98.8 | 32.3 |
| 8112 | 63.1 | 744 | 702 | 696 | 100.0 | 99.1 | 99.1 | 93.6 |
| AVERAGE | 70.6 | | | | 91.9 | 97.6 | 98.0 | 85.2 |

SOUTHERN INDIANA GAS & ELEC
A.B. BROWN
1

NET GENERATING CAPACITY WITH FGD = 250
GROSS GENERATING CAPACITY = 265
% SCRUBBED = 100

| DATE | CAPACITY FACTOR | PERIOD HOURS | BOILER HOURS | FGD HOURS | AVAILABILITY | OPERABILITY | RELIABILITY | UTILIZATION |
|---|---|---|---|---|---|---|---|---|
| 8101 | 61.8 | 744 | 744 | 736 | 99.3 | 98.9 | 98.9 | 98.9 |
| 8102 | 56.8 | 672 | 672 | 667 | 99.3 | 99.3 | 99.3 | 99.3 |
| 8103 | 59.8 | 744 | 731 | 630 | 93.6 | 86.1 | 88.2 | 84.6 |
| 8104 | 5.5 | 720 | 87 | 0 | 100.0 | 0.0 | *** | 0.0 |
| 8105 | 35.9 | 744 | 464 | 376 | 87.7 | 81.0 | 82.4 | 50.5 |
| 8106 | 63.0 | 720 | 708 | 699 | 99.9 | 98.6 | 99.1 | 97.0 |
| 8107 | 62.5 | 744 | 744 | 627 | 91.4 | 84.3 | 87.4 | 84.3 |
| 8108 | 52.6 | 744 | 741 | 662 | 92.3 | 89.4 | 89.4 | 89.0 |
| 8109 | 45.5 | 720 | 668 | 650 | 97.5 | 97.3 | 90.3 | 90.3 |
| 8110 | 53.0 | 744 | 670 | 628 | 98.2 | 93.7 | 94.1 | 84.4 |
| 8111 | 49.7 | 720 | 720 | 654 | 92.6 | 90.9 | 90.9 | 90.9 |
| 8112 | 32.0 | 744 | 456 | 286 | 97.5 | 62.7 | 62.7 | 38.4 |
| AVERAGE | 48.1 | | | | 95.8 | 81.8 | 89.3 | 75.6 |

NOTE: *'S INDICATE THAT THE VALUE DOES NOT EXIST.

TABLE 4-1b. FGDIS FIELDS FOR PREPARATION OF TABLE 4-1a.

IDENTIFICATION NUMBER
FOREIGN - DOMESTIC
$SO_2$ & PARTICLE/PARTICLE
COMPANY NAME
PLANT NAME
UNIT NUMBER
NET UNIT GENERATING CAPACITY WITH FGD - MW
GROSS UNIT GENERATING CAPACITY - MW
EQUIVALENT SCRUBBED CAPACITY
PERFORMANCE DATE - YYMM
UNIT CAPACITY FACTOR - %
PERIOD - HR
BOILER - HR
SERVICE - HR
MODULE NUMBER
MODULE AVAILABILITY
MODULE OPERABILITY
MODULE RELIABILITY
MODULE UTILIZATION

Availability data for operating FGD systems have been collected through the EPA Utility FGD Survey program on a monthly basis. The monthly data were used to calculate the average annual availabilities for each system.

Figures 4-1a, 4-1b, and 4-1c are the median analyses of the annual average availabilities for all low-, medium-, and high-sulfur coal operations, respectively for which availability data has been obtained. These annual averages are based on at least six months of data, annual average with less than six months of data are not considered. Median analyses were based on data from the period of 1978 through 1981. In each case, the availability points were plotted and the median was determined. A dashed line connects the median point for each year.

As can be seen from Figure 4-1a, low sulfur systems show the steadiest median of the three with the median changing only a few percentage points. The medium- and high-sulfur systems show an overall increase from 1978 to 1981, however, fluctuations are observed for the medium-sulfur systems between 1979 and 1980.

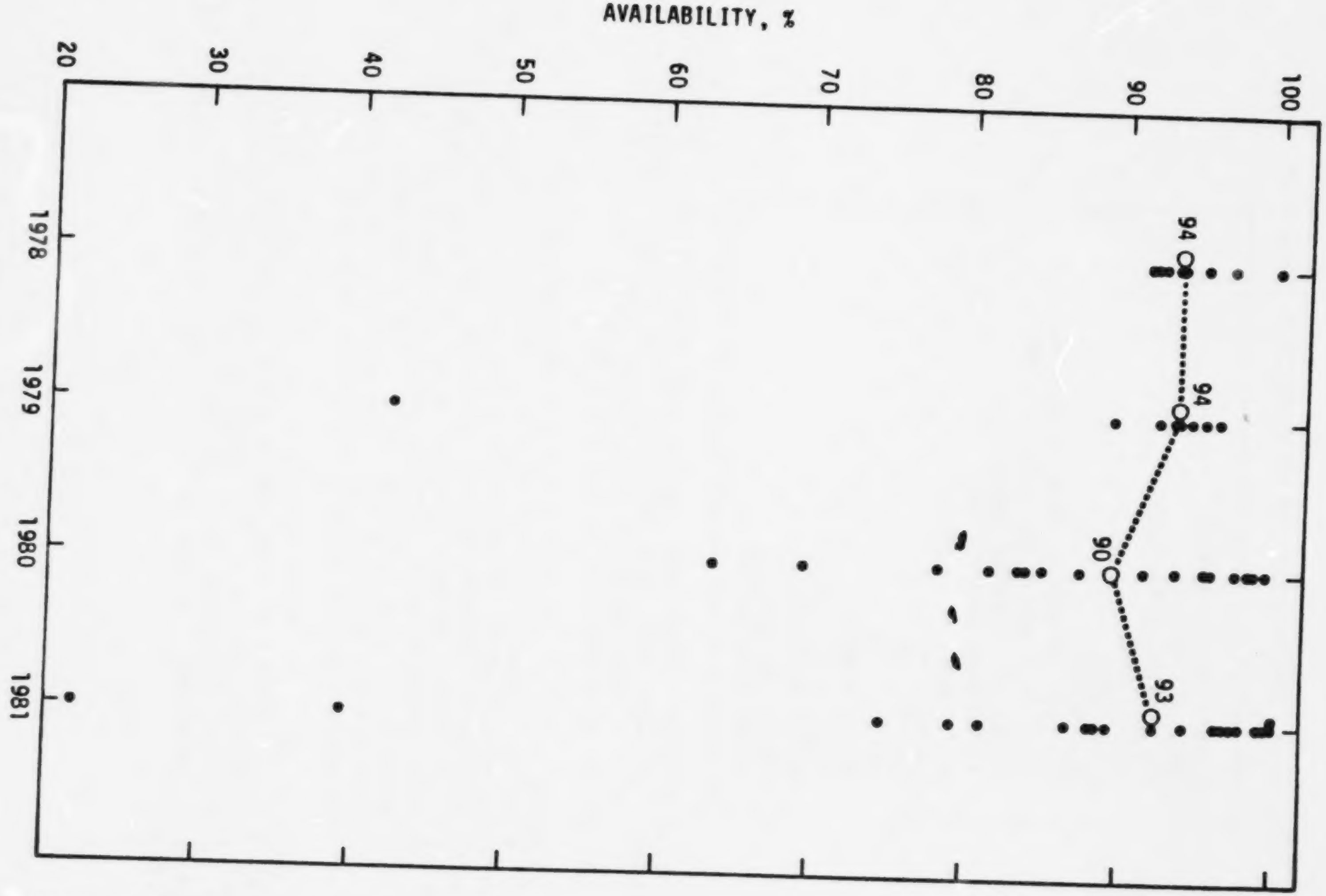


Figure 4-1a. Median analyses of the average annual availability data for low-sulfur coal operations between the years 1978 and 1981.

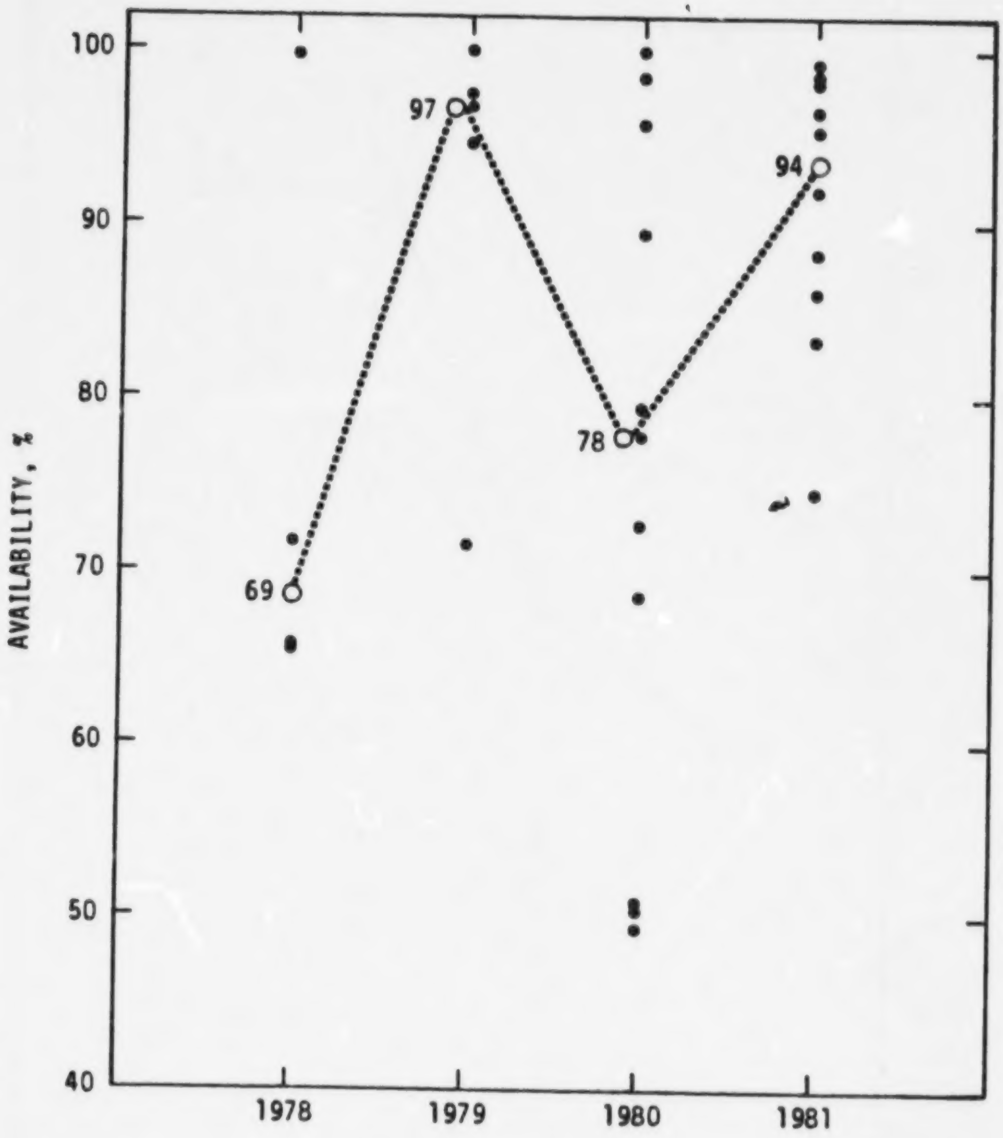


Figure 4-1b. Median analyses of the average annual availability data for medium-sulfur coal operations between the years 1978 and 1981.

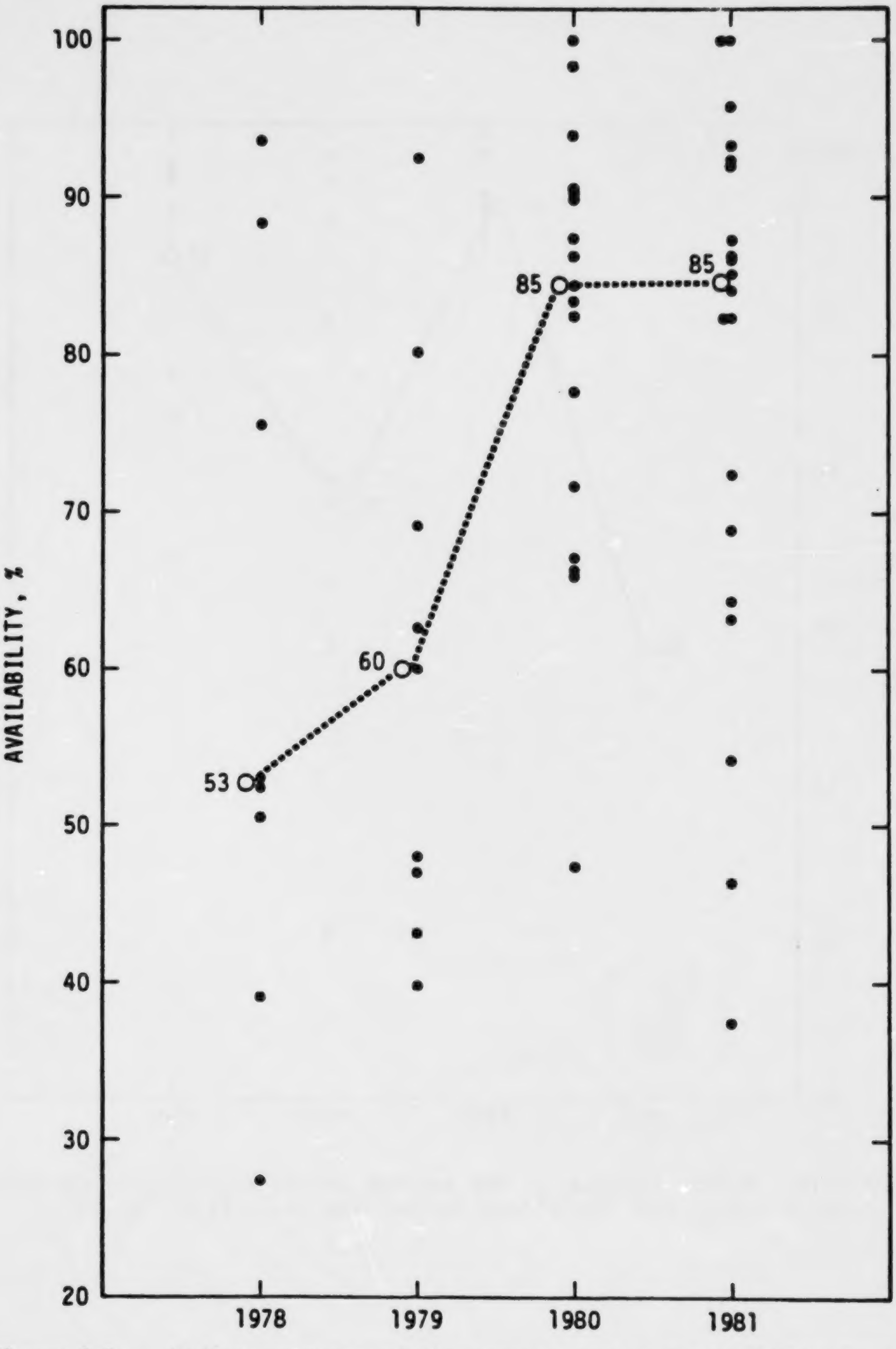


Figure 4-1c. Median analyses of the average annual availability data for high-sulfur coal operations between the years 1978 and 1981.

# SECTION 5

# CAPITAL AND ANNUAL COSTS

Another activity of the utility survey program is the acquisition and analysis of cost data. In this activity, emphasis is placed on costs associated with operational systems because of the availability of meaningful and complete data. These data are adjusted only to ensure their completeness and accuracy and to facilitate comparison.

Capital and annual cost data for operational FGD systems have been obtained continuously since March 1978. Costs for each system are obtained directly from the utilities and then itemized by individual FGD cost element. The itemized costs are then adjusted to a common basis to enhance comparability. This adjustment includes factors for estimating costs not given by the utilities and escalating all costs to common dollars (mid-1981). All adjusted cost data and computations are reviewed and verified with the appropriate utility before publication.

A summary of the cost adjustment procedure is shown below.

## Capital Costs

- All costs associated with control of particulate matter emissions are excluded.
- Capital costs for modifications necessitated by installation of an FGD system are added if they were not included in the reported costs.
- Sludge disposal costs are adjusted to reflect a 20-year life span for retrofit systems and a 30-year life span for new systems.
- Any unreported direct and indirect costs incurred are estimated and included.
- All capital costs are escalated to mid-1981 dollars.
- All $/kW values reflect the gross generating capacity of the unit.

## Annual Costs

- All costs are adjusted to a common 65% capacity factor.
- Direct costs that were not reported are estimated and added.
- Overhead and fixed costs that were not reported are estimated and added.
- All annual costs are escalated to mid-1981 dollars.
- All mills/kWh values are based on a 65% capacity factor and the net generating capacity of the unit.

Table 5-1a summarizes both reported and adjusted costs for all operational FGD systems on which cost data were obtained. This table also summarizes the results by application (NEW/RETROFIT) and by sulfur content of the coal (high sulfur/low sulfur). Table 5-1a was prepared from the FGDIS data fields shown in Table 5-1b. NEW/RETROFIT and SALABLE PRODUCT/THROWAWAY PRODUCT were accessed via Level 1 at the top of the FGD GENERAL DATA "tree".

Table 5-2a lists the results by process type. The data fields shown in Table 5-2b were used to generate Table 5-2a. PROCESS TYPE is found in Level 1 under FGD GENERAL DATA. The three remaining fields are found in Level 2 of this "tree" under ECONOMICS DATA. The three remaining fields are found in Level 2 of this same "tree" under the heading ECONOMICS DATA.

Table 5-3 provides a plant-by-plant listing of the reported and adjusted costs for the operational FGD systems addressed in this study.

TABLE 5-1a. CATEGORICAL RESULTS OF THE REPORTED AND ADJUSTED CAPITAL AND ANNUAL COSTS FOR OPERATIONAL FGD SYSTEMS

| | Reported | | | | | | Adjusted | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Capital | | | Annual | | | Capital | | | Annual | | |
| | Range, $/kW | Average, $/kW | α | Range, mills/kWh | Average, mills/kWh | α | Range, $/kW | Average, $/kW | α | Range, mills/kWh | Average, mills/kWh | α |
| All | 23.7-213.6 | 80.2 | 44.3 | 0.1-13.0 | 2.3 | 2.8 | 38.3-282.2 | 118.8 | 58.1 | 1.6-20.8 | 7.6 | 4.1 |
| New | 23.7-213.6 | 80.4 | 46.1 | 0.1-5.5 | 1.7 | 1.8 | 38.3-263.9 | 110.8 | 48.4 | 1.6-14.6 | 6.8 | 3.2 |
| Retrofit | 29.4-157.4 | 79.7 | 39.4 | 0.5-13.0 | 4.5 | 4.4 | 60.4-282.2 | 139.3 | 73.8 | 4.3-20.8 | 9.7 | 5.3 |
| Saleable | 132.8-185.0 | 153.1 | 20.6 | 13.0-13.0 | 13.0 | 0.0 | 254.6-282.2 | 271.6 | 12.1 | 16.7-20.8 | 18.1 | 1.9 |
| Throwaway | 23.7-213.6 | 75.8 | 41.5 | 0.1-11.3 | 2.1 | 2.4 | 38.3-263.9 | 110.9 | 47.6 | 1.6-17.6 | 7.0 | 3.4 |

TABLE 5-1b. FGDIS FIELDS FOR GENERATION OF TABLE 5-1a.

NEW/RETROFIT
SALABLE PRODUCT/THROWAWAY PRODUCT
ECONOMICS TYPE - REPORTED/ADJUSTED/STANDARDIZED
TOTAL $/kW
TOTAL MILLS/kWh

TABLE 5-2a. ADJUSTED CAPITAL AND ANNUAL COSTS FOR OPERATIONAL FGD SYSTEMS BY PROCESS TYPE

| | Reported | | | | | | Adjusted | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Capital | | | Annual | | | Capital | | | Annual | | |
| | Range, $/kW | Average, $/kW | $\sigma$ | Range, mills/kWh | Average, mills/kWh | $\sigma$ | Range, $/kW | Average, $/kW | $\sigma$ | Range, mills/kWh | Average, mills/kWh | $\sigma$ |
| Limestone | 23.7-170.4 | 67.9 | 37.2 | 0.1-7.8 | 1.6 | 2.2 | 38.3-194.3 | 98.9 | 44.0 | 1.6-14.6 | 6.1 | 3.1 |
| Lime | 29.4-213.6 | 81.8 | 43.7 | 0.3-11.3 | 3.2 | 2.7 | 60.4-210.0 | 116.5 | 44.2 | 4.0-17.6 | 8.1 | 3.6 |
| Dual alkali | 47.2-174.8 | 97.8 | 55.3 | 1.3-1.3 | 1.3 | 0.0 | 87.8-263.9 | 146.7 | 82.9 | 5.0-13.9 | 8.7 | 3.8 |
| Lime/alkaline flyash | 43.4-173.8 | 93.9 | 44.0 | 0.4-5.4 | 2.1 | 1.9 | 52.5-184.4 | 122.8 | 51.4 | 3.0-14.1 | 7.2 | 3.8 |
| Sodium carbonate | 42.9-100.8 | 69.2 | 26.2 | 0.2-0.5 | 0.4 | 0.1 | 87.1-150.9 | 110.9 | 26.4 | 5.8-7.4 | 6.4 | 0.7 |
| Wellman-Lord | 132.8-185.0 | 153.1 | 20.6 | 13.0-13.0 | 13.0 | 0.0 | 254.6-282.2 | 271.6 | 12.1 | 16.7-20.8 | 18.1 | 1.9 |
| Limestone/alkaline flyash | 49.3-49.3 | 49.3 | 0.0 | 0.8-0.8 | 0.8 | 0.0 | 102.6-102.6 | 102.6 | 0.0 | 5.4-5.4 | 5.4 | 0.0 |

TABLE 5-2b. FGDIS FIELDS FOR GENERATION OF TABLE 5-2a.

PROCESS TYPE - LIME/LIMESTONE/ETC.
ECONOMICS TYPE - REPORTED/ADJUSTED/STANDARDIZED
TOTAL $/kW
TOTAL MILLS/kWh

# TABLE 5-3. REPORTED AND ADJUSTED CAPITAL AND ANNUAL COSTS FOR OPERATIONAL FGD SYSTEMS

| | Reported | | | | Adjusted | | | |
|---|---|---|---|---|---|---|---|---|
| | Capital | $/kW | Annual | Mills/kWh | Capital | $/kW | Annual | Mills/kWh |
| Alabama Electric | | | | | | | | |
| Tombigbee 2 | 6,921,100 | 27.4 | 434,929 | 0.33 | 9,756,200 | 38.3 | 4,249,650 | 3.18 |
| Tombigbee 3 | 6,992,100 | 27.4 | 434,929 | 0.33 | 9,756,200 | 38.3 | 4,249,650 | 3.18 |
| Arizona Electric Power | | | | | | | | |
| Apache 2 | 8,148,069 | 41.8 | 51,784 | 0.10 | 13,171,700 | 67.5 | 3,739,900 | 3.75 |
| Apache 3 | 7,214,052 | 37.0 | 51,784 | 0.10 | 11,661,900 | 59.8 | 3,739,900 | 3.75 |
| Arizona Public Service | | | | | | | | |
| Cholla 1 | 6,550,000 | 52.0 | NA | NA | 10,246,100 | 81.3 | 4,608,800 | 4.79 |
| Cholla 2 | 44,352,000 | 168.0 | 1,003,568 | 0.75 | 42,787,600 | 162.1 | 10,998,300 | 8.22 |
| Central Illinois Light | | | | | | | | |
| Duck Creek 1 | 31,125,000 | 74.8 | 10,851,000 | 5.04 | 55,001,000 | 132.2 | 12,433,100 | 5.78 |
| Central Illinois Public Service | | | | | | | | |
| Newton 1 | 107,831,000 | 174.8 | NA | NA | 162,847,600 | 263.9 | 45,624,900 | 13.94 |
| Colorado Ute Electric | | | | | | | | |
| Craig 1 | 38,613,500 | 86.5 | 462,600 | 0.53 | 48,179,000 | 105.9 | 12,148,300 | 5.33 |
| Craig 2 | 32,810,500 | 73.5 | 1,128,400 | 0.48 | 41,070,100 | 90.3 | 10,382,700 | 4.56 |
| Columbus & Southern Ohio Electric | | | | | | | | |
| Conesville 5 | 20,663,500 | 50.3 | 8,670,530 | 5.52 | 40,857,200 | 99.4 | 14,475,100 | 6.78 |
| Conesville 6 | 20,663,500 | 50.3 | 8,670,530 | 5.52 | 40,857,200 | 99.4 | 14,475,100 | 6.78 |
| Cooperative Power Association | | | | | | | | |
| Coal Creek 1 | 23,650,000 | 43.4 | 1,166,200 | 0.41 | 28,633,100 | 52.5 | 8,414,350 | 2.99 |
| Coal Creek 2 | 23,650,000 | 43.4 | 1,166,200 | 0.41 | 28,633,100 | 52.5 | 8,414,350 | 2.99 |
| Duquesne Light | | | | | | | | |
| Elrama 1-4 | 61,320,000 | 120.2 | 21,027,451 | 7.18 | 95,755,400 | 187.8 | 35,731,700 | 12.89 |
| Phillips 1-6 | 52,055,000 | 127.0 | 18,301,000 | 11.00 | 86,097,500 | 210.0 | 35,731,700 | 17.65 |
| Indianapolis Power & Light | | | | | | | | |
| Petersburg 3 | 55,820,000 | 104.9 | NA | NA | 86,227,500 | 162.1 | 28,565,000 | 9.74 |
| Kansas City Power & Light | | | | | | | | |
| Hawthorn 3 | 3,220,000 | 29.4 | 346,441 | 1.15 | 6,909,850 | 62.8 | 2,912,100 | 5.25 |
| Hawthorn 4 | 3,220,000 | 29.4 | 346,441 | 1.15 | 6,909,850 | 62.8 | 2,912,100 | 5.25 |
| LaCygne 1 | 46,900,000 | 53.7 | 8,060,047 | 5.38 | 87,498,400 | 100.1 | 52,735,300 | 11.29 |
| Kansas Power & Light | | | | | | | | |
| Jeffrey 1 | 27,306,900 | 37.9 | 321,000 | 0.11 | 39,710,500 | 55.9 | 9,353,200 | 2.42 |
| Jeffrey 2 | 26,458,800 | 37.8 | 949,900 | 0.29 | 28,840,100 | 41.2 | 6,396,400 | 1.65 |
| Kentucky Utilities | | | | | | | | |
| Green River 1-3 | 3,966,155 | 62.0 | 364,005 | 5.20 | 7,510,600 | 117.8 | 3,754,800 | 10.99 |
| Louisville Gas & Electric | | | | | | | | |
| Cane Run 4 | 12,647,000 | 66.6 | 960,301 | 1.29 | 21,882,500 | 115.2 | 6,422,400 | 6.20 |
| Cane Run 5 | 13,759,000 | 68.8 | 763,443 | 0.92 | 20,476,600 | 102.4 | 5,784,300 | 5.30 |
| Cane Run 6 | 20,596,900 | 71.5 | NA | NA | 25,290,600 | 87.8 | 11,073,000 | 7.23 |
| Mill Creek 1 | 17,661,500 | 55.0 | NA | NA | 21,627,800 | 60.4 | 8,107,100 | 4.26 |
| Mill Creek 3 | 18,846,880 | 42.6 | 321,463 | 1.25 | 29,163,000 | 66.0 | 9,636,200 | 4.03 |
| Paddy's Run 6 | 4,320,000 | 61.7 | NA | NA | 9,307,300 | 133.0 | 4,430,300 | 12.25 |
| Minnesota Power & Light | | | | | | | | |
| Clay Boswell 4 | 86,900,000 | 173.8 | 18,844,512 | 5.38 | 102,165,300 | 184.4 | 40,437,300 | 14.09 |
| Minnkota Power | | | | | | | | |
| Milton R. Young 2 | 44,119,600 | 100.3 | 754,445 | 0.53 | 68,487,500 | 155.7 | 14,966,000 | 6.44 |
| Monongahela Power | | | | | | | | |
| Pleasants 1 | 81,452,400 | 119.1 | 5,532,800 | 1.46 | 104,562,000 | 152.9 | 27,951,300 | 7.94 |
| Pleasants 2 | 81,452,400 | 119.1 | 5,532,800 | 1.46 | 104,562,000 | 152.9 | 27,951,300 | 7.94 |
| Montana Power | | | | | | | | |
| Colstrip 1 | 36,500,000 | 101.4 | 6,128,000 | 2.97 | 52,519,850 | 145.9 | 15,642,050 | 8.27 |
| Colstrip 2 | 36,500,000 | 101.4 | 6,128,000 | 2.97 | 52,519,850 | 145.9 | 15,642,050 | 8.27 |
| Nevada Power | | | | | | | | |
| Reid Gardner 1 | 5,363,375 | 42.9 | 251,514 | 0.46 | 10,891,350 | 87.1 | 3,617,450 | 5.78 |
| Reid Gardner 2 | 5,363,375 | 42.9 | 251,514 | 0.46 | 10,891,350 | 87.1 | 3,617,450 | 5.78 |
| Reid Gardner 3 | 12,599,160 | 100.8 | 131,824 | 0.23 | 18,866,173 | 150.9 | 4,637,163 | 7.40 |
| Northern Indiana Public Service | | | | | | | | |
| Dean H. Mitchell 11 | 18,192,040 | 157.4 | 2,414,589 | 13.02 | 29,431,808 | 254.6 | 11,129,239 | 20.79 |
| Northern States Power | | | | | | | | |
| Sherburne 1 | 34,892,020 | 49.3 | 2,716,759 | 0.75 | 73,854,486 | 102.6 | 21,018,195 | 5.43 |
| Sherburne 2 | 34,982,020 | 49.3 | 2,716,759 | 0.75 | 73,854,486 | 102.6 | 21,018,195 | 5.43 |
| Pacific Power & Light | | | | | | | | |
| Jim Bridger 4 | 49,643,000 | 90.3 | NA | NA | 65,113,736 | 118,4 | 19,681,160 | 6.81 |
| Pennsylvania Power | | | | | | | | |
| Bruce Mansfield 1 | 110,639,000 | 120.7 | 9,979,900 | 3.28 | 132,234,039 | 144.2 | 53,122,918 | 11.31 |
| Bruce Mansfield 2 | 110,639,000 | 120.6 | 9,979,900 | 3.28 | 132,234,039 | 144.2 | 53,122,918 | 11.31 |
| Bruce Mansfield 3 | 195,857,200 | 213.6 | 11,575,300 | 3.11 | 166,043,400 | 181.1 | 48,255,200 | 10.27 |
| Public Service of New Mexico | | | | | | | | |
| San Juan 1 | 47,944,400 | 132.8 | NA | NA | 100,333,473 | 277.9 | 29,836,802 | 16.69 |
| San Juan 2 | 47,985,000 | 137.1 | NA | NA | 98,777,569 | 282.2 | 29,423,764 | 16.89 |
| Salt River Project | | | | | | | | |
| Coronado 1 | 32,624,500 | 79.4 | 1,788,000 | 0.85 | 35,560,700 | 86.5 | 15,339,100 | 7.70 |
| Coronado 2 | 32,624,500 | 79.4 | 1,788,000 | 0.85 | 35,560,700 | 86.5 | 15,339,100 | 7.70 |
| South Carolina Public Service | | | | | | | | |
| Winyah 2 | 6,646,098 | 23.7 | 527,000 | 0.29 | 13,148,872 | 47.0 | 2,697,896 | 1.84 |
| Winyah 3 | 10,742,500 | 38.4 | NA | NA | 18,646,700 | 66.6 | 6,926,700 | 4.83 |
| South Mississippi Electric Power | | | | | | | | |
| R.D. Morrow, Sr. 1 | 10,896,000 | 53.7 | NA | NA | 24,047,200 | 118.5 | 7,115,990 | 6.94 |
| R.D. Morrow, Sr. 2 | 10,896,000 | 53.7 | NA | NA | 24,047,200 | 118.5 | 7,115,990 | 6.94 |
| Southern Illinois Power | | | | | | | | |
| Marion 4 | 15,200,930 | 87.9 | 859,453 | 0.98 | 20,906,447 | 120.8 | 7,107,823 | 7.75 |
| Southern Indiana Gas & Electric | | | | | | | | |
| A.B. Brown 1 | 12,495,000 | 47.2 | 1,850,565 | 1.30 | 23,414,388 | 88.4 | 7,094,130 | 4.98 |
| Springfield City Utilities | | | | | | | | |
| Southwest 1 | 16,744,500 | 86.3 | 778,749 | 1.20 | 27,822,607 | 143.4 | 8,092,238 | 8.21 |
| Springfield Water, Light & Power | | | | | | | | |
| Dallman 3 | 34,923,800 | 170.4 | 4,381,500 | 4.68 | 39,829,200 | 194.3 | 15,913,700 | 14.56 |
| Tennessee Valley Authority | | | | | | | | |
| Widows Creek 8 | 47,900,000 | 87.1 | 14,576,400 | 7.76 | 86,968,828 | 158.1 | 21,379,073 | 7.28 |
| Utah Power & Light | | | | | | | | |
| Hunter 1 | 24,400,000 | 56.7 | NA | NA | 32,294,620 | 75.1 | 10,614,532 | 4.66 |
| Hunter 2 | 25,880,000 | 60.2 | 1,072,600 | 0.32 | 31,225,000 | 72.6 | 10,355,700 | 4.55 |
| Huntington 1 | 2,709,000 | 63.0 | 2,946,400 | 1.27 | 38,698,607 | 90.0 | 13,411,652 | 5.89 |

NA - Annual costs not available from the utility.

# ECONOMIC EVALUATION AND COMPARISON OF ALTERNATIVE LIMESTONE SCRUBBING OPTIONS

By

T. A. Burnett, R. L. Torstrick, and F. A. Sudhoff
Division of Energy Demonstrations and Technology
Office of Power
Tennessee Valley Authority
Muscle Shoals, Alabama

## ABSTRACT

The preliminary-grade economics (accuracy: -15%, +30%) of various alternative limestone scrubbing options (absorber type, with and without forced oxidation, and with and without adipic acid enhancement) are examined using the current design and economic premises established for the continuing series of economic evaluations performed by TVA for EPA. The economics are projected using the Shawnee lime/limestone computer model, which is based on long-term operating data from the EPA Alkali Scrubbing Test Facility at the TVA Shawnee Steam Plant near Paducah, Kentucky. The capital investment for the base-case limestone scrubbing process (500 MW, 3.5% sulfur coal, 1979 NSPS, spray tower, forced oxidation, landfill) is $206/kW. The first-year and levelized annual revenue requirements are 10.59 and 15.09 mills/kWh respectively. Costs for the equivalent limestone scrubbing process using a Turbulent Contact Absorber (TCA) are lower while those for the venturi - spray tower absorber are higher. The forced-oxidation landfill disposal option has a lower capital investment than the unoxidized pond disposal option for all cases studied; however, the first-year and levelized annual revenue requirements are slightly higher for the forced-oxidation landfill process for most coal applications. For the spray tower limestone process to achieve a specified $SO_2$ removal efficiency, it is more economical to increase the limestone stoichiometry and minimize the absorber L/G. The use of adipic acid or possibly dibasic acid (DBA) as an additive to enhance $SO_2$ removal in the limestone scrubbing process is an economically attractive option. The use of adipic acid remains economically attractive even if both a high unit cost and a high degradation factor for adipic acid are assumed.

# ECONOMIC EVALUATION AND COMPARISON OF ALTERNATIVE LIMESTONE SCRUBBING OPTIONS

## INTRODUCTION

Recently TVA initiated an economic evaluation of advanced concepts in limestone and lime flue gas desulfurization (FGD) technology. The evaluation is part of a continuing program of utility FGD economic evaluations that TVA has conducted for EPA since 1967. The limestone FGD technology evaluated in this paper is based on tests conducted at the EPA Alkali Scrubbing Test Facility at the TVA Shawnee Steam Plant near Paducah, Kentucky.

The EPA Alkali Scrubbing Test Facility originally consisted of three prototype-size scrubber units, each capable of processing about 30,000 aft$^3$/min (10 MW equivalent) of flue gas. For the past 10 years it has been used to develop and evaluate limestone and lime FGD technology (1). One unit, a marble-bed absorber, was shut down in 1973 and converted to a cocurrent absorber in 1978. The other two units, a mobile-bed absorber (Turbulent Contact Absorber or TCA) and a venturi - spray tower, have been operated under a variety of conditions since 1972. Until December 1980 this test program was funded by EPA. It was operated by TVA with Bechtel National, Inc., serving as technical director for EPA. Using this test facility data, TVA and Bechtel developed a computer model (the Shawnee lime/limestone computer model) that projects the design and costs for full-sized limestone and lime FGD systems (2).

The computer model was used in this evaluation to calculate the economics of the numerous limestone scrubbing process variations (types of absorber, waste disposal methods, absorber design conditions, forced oxidation, and the use of additives) that have been developed or evaluated at the test facility. The results of the evaluation discussed in this paper will be published in a report by TVA and EPA in the near future. In addition to established limestone scrubbing processes, part of the evaluation dealt with the use of additives such as adipic acid or dibasic acid (DBA) to enhance the efficiency of limestone scrubbing slurries. The results for both established limestone scrubbing processes and those enhanced with adipic acid and DBA are discussed in this paper.

The chemistry and practical aspects of organic acid buffers in limestone scrubbing FGD have been discussed by Hatfield et al. (3), Rochelle (4), and Rochelle and King (5). The evaluation of adipic acid as such an additive, which was begun by EPA in 1978 and which constituted a major portion of the test facility studies from 1978 to 1980, has been reported by Head and others (6) and Burbank et al. (7).

From an economic standpoint, when incorporated into the design of new FGD systems, the use of adipic acid offers two possibilities for cost reductions. First, the improved $SO_2$ removal efficiency may permit the use of smaller or less complicated absorbers, lower L/G ratios, and lower stoichiometries. Also less limestone may be consumed and therefore less waste may be produced. Second, the improved $SO_2$ removal efficiency may permit alternate designs, such as partial scrubbing and bypass, which are often not adequate or practical with unenhanced limestone processes. All of these considerations are addressed in this paper. Other economic benefits such as upgrading the performance of existing units to avoid more costly alternatives are also possible.

## DESIGN AND ECONOMIC PREMISES

The major design and economic premises for this study are shown in Table 1. The economic evaluations are based on FGD systems designed to meet the 1979 new-source performance standards (NSPS) for a new, pulverized-coal-fired utility boiler. Three boiler sizes and three different coals are used. The FGD systems are designed based on the assumption that 92% of the sulfur in the coal is emitted as $SO_x$ (some regulations are based on 95% which would have only a minor effect on the process economics). The FGD systems are also designed with one spare scrubber train, a spare feed preparation train, and 50% emergency flue gas bypass. The power plant is assumed to have a 30-year, 165,000-hour life and to operate 5,500 hours/year.

TABLE 1. MAJOR DESIGN AND ECONOMIC PREMISES

| Item | Premise |
|---|---|
| Power plant | 200-MW, 500-MW, 1,000-MW new, pulverized-coal-fired boilers |
| Fuel | |
| Eastern bituminous, 2.0% S | 11,700 Btu/lb, 15.1% ash, 4.0% moisture, 2.0% sulfur (dry basis) |
| Eastern bituminous, 3.5% S | 11,700 Btu/lb, 15.1% ash, 4.0% moisture, 3.5% sulfur (dry basis) |
| Eastern bituminous, 5.0% S | 11,700 Btu/lb, 15.1% ash, 4.0% moisture, 5.0% sulfur (dry basis) |
| Operating schedule | 165,000 hr, 30-year life; 5,500-hr first-year operation |
| Waste disposal area | Clay-lined pond or landfill located one mile from the FGD facility |
| $SO_2$ removal efficiency | Revised 1979 NSPS |
| Spare equipment | |
| Feed preparation area | One spare train |
| $SO_2$ absorption area | One spare train |
| Base Year | |
| Capital investment | Mid-1982 |
| Revenue requirements | Mid-1984 |

## Design Premises

Absorber Options--

A variety of absorber types and combinations have been used in limestone FGD, a diversity reflecting the numerous different approaches to efficient and practical processes. From the inception of FGD, conventional packed absorbers found limited application in limestone scrubbing, primarily because of scaling and plugging, particularly if operated at the low liquid rates their high efficiency permits. In an effort to alleviate the scaling and plugging problems of packed beds, several types of mobile-bed absorbers have been used in FGD applications. One is the TCA which was installed at the test facility as well as other locations. The continuing problems of scaling and plugging have led to increasing use of absorbers with simple internal designs, such as a venturi - spray tower or more recently a spray tower only. All three types of absorbers, a TCA, a venturi - spray tower, and a spray tower are used as a basis of a limestone scrubbing process, the relative economics of which are then compared.

The absorber design conditions (and thus indirectly the economic results) presented in this paper are based on equations generated by Bechtel National to model the data developed during operation of the EPA Alkali Scrubbing Test Facility. Thus the specified conditions do not necessarily reflect the views of either TVA or the various vendors who supply limestone FGD systems to the utility industry. These absorber design conditions are shown in Table 2. Brief descriptions of these three types of absorbers are given below.

TABLE 2. DESIGN CONDITIONS FOR EACH ABSORBER TYPE

(500 MW, 3.5% sulfur in coal, revised 1979 NSPS,

onsite waste disposal)

| | Absorber type | | |
|---|---|---|---|
| | TCA | Spray tower | Venturi - spray tower |
| Presaturator | | | |
| Type | Spray chamber | Spray chamber | Venturi |
| L/G, gal/kaft$^3$ | 4 | 4 | 20 |
| Absorber | | | |
| Gas velocity, ft/sec | 12.5 | 10 | 10 |
| L/G, gal/kaft$^3$ | 58 | 106 | 103 |
| Stoichiometry, mol $CaCO_3$/ mol $SO_2$ absorbed | 1.43 | 1.40 | 1.3 |
| Pressure drop (absorber + presaturator), inches of $H_2O$ | 9.0 | 2.6 | 11.5 |
| Total pressure drop, inches of $H_2O$ | 15.2 | 7.9 | 18.0 |

TCA--The TCA has been one of the more successful mobile-bed absorbers applied to FGD, particularly in the mid-1970's. Recently, however, the TCA has lost favor with the utility industry and has been to a large extent replaced by the spray tower which will be discussed later. The basic design consists of a countercurrent vertical absorber in which the gas moves upward through successive beds of light weight spheres confined between grids. The sphere beds are placed in turbulent motion by the gas and expand to fill the space between the confining grids.

The TCA used in the model has a presaturator into which scrubbing liquid at an L/G ratio of 4 gal/kaft$^3$ is sprayed to cool and humidify the gas. The TCA is constructed of neoprene-lined carbon steel and contains four 316L stainless steel grids spaced 4 feet apart to form three absorber beds. Each bed is packed with nitrile foam spheres to a static depth of 5 inches. A single bank of sprays above the top bed distributes the absorbent liquid in the absorber. A horizontal, three-pass, open-vane, fiberglass, chevron-type mist eliminator above the absorbers is provided to minimize entrained moisture.

Venturi - Spray Tower--The venturi scrubber used in the venturi - spray tower combination is a single-stage venturi with a movable axial plug. It is constructed of 316 stainless steel and has an acid-brick-lined throat. Flue gas enters horizontally into the top of the vertically mounted venturi and flows downward through the throat. Absorbent liquid is injected into the area above the throat through a peripheral annulus and an axial spray. The venturi is mounted over a catch basin that drains to the hold tank. Flue gas leaves the venturi horizontally and enters the bottom of the spray tower as described below. For the venturi - spray tower alternative, the venturi serves as the presaturator.

Spray Tower--The spray tower is a countercurrent vertical absorber in which the gas moves upward through the absorber. The spray tower is a hollow shell with a rectangular cross section and essentially no internal structure other than spray headers. When used alone it has a presaturator section similar to that used in the TCA. The spray tower is constructed of neoprene-lined carbon steel and has four 316L stainless steel grids like those in the TCA to control gas distribution. Four banks of sprays are used for the absorbent liquid distribution, one above each of the top three grids spraying downward, and one below the bottom grid spraying upward. A horizontal, chevron-type mist eliminator (the same design as in the TCA) is situated at the top of the tower.

Oxidation and Additive Enhancement Options--In addition to variations in the type of absorber used, the scrubbing system can be operated in one of three ways: no forced oxidation with ponding, forced oxidation to gypsum with dewatering and landfill, or forced oxidation with adipic acid addition, dewatering, and landfill. [For terminology sake, the forced oxidation to gypsum with dewatering and landfill system will be referred to as the base-case limestone process, the forced oxidation with adipic acid addition, dewatering, and landfill system will be referred to as the advanced limestone process, and the unoxidized ponding system will be referred to as the conventional limestone process.] The spray tower design conditions are shown in Table 3 for these processes. A flow diagram for the base-case limestone process is shown in Figure 1.

### TABLE 3. SPRAY TOWER ABSORBER DESIGN CONDITIONS FOR ALTERNATE LIMESTONE SCRUBBING SYSTEMS

(500 MW, 3.5% sulfur in coal, revised 1979 NSPS, onsite waste disposal)

| | Spray tower absorber design conditions | | |
|---|---|---|---|
| | Conventional limestone[a] | Base-case limestone[b] | Advanced limestone[c] |
| Absorber gas velocity, ft/sec | 10 | 10 | 10 |
| $SO_2$ removal efficiency in the absorber, % | 88.7 | 88.7 | 95 |
| Overall $SO_2$ removal in the FGD system, % | 88.7 | 88.7 | 88.7 |
| L/G, gal/kaft$^3$ | 106 | 106 | 80 |
| Stoichiometry, mol $CaCO_3$/mol $SO_2$ absorbed | 1.4 | 1.4 | 1.07 |
| Adipic acid concentration, ppm | - | - | 1,500 |
| Air stoichiometry, mols O/mol $SO_2$ absorbed | - | 2.5 | 2.5 |
| Sulfite oxidation, % | 30 | 95 | 95 |
| Bypass | | | |
| Normal, % | - | - | 6.4 |
| Emergency, % | 50 | 50 | 50 |

a. Spray tower, no forced-oxidation, pond.
b. Spray tower, forced-oxidation, landfill.
c. Spray tower, forced-oxidation, adipic acid, landfill.

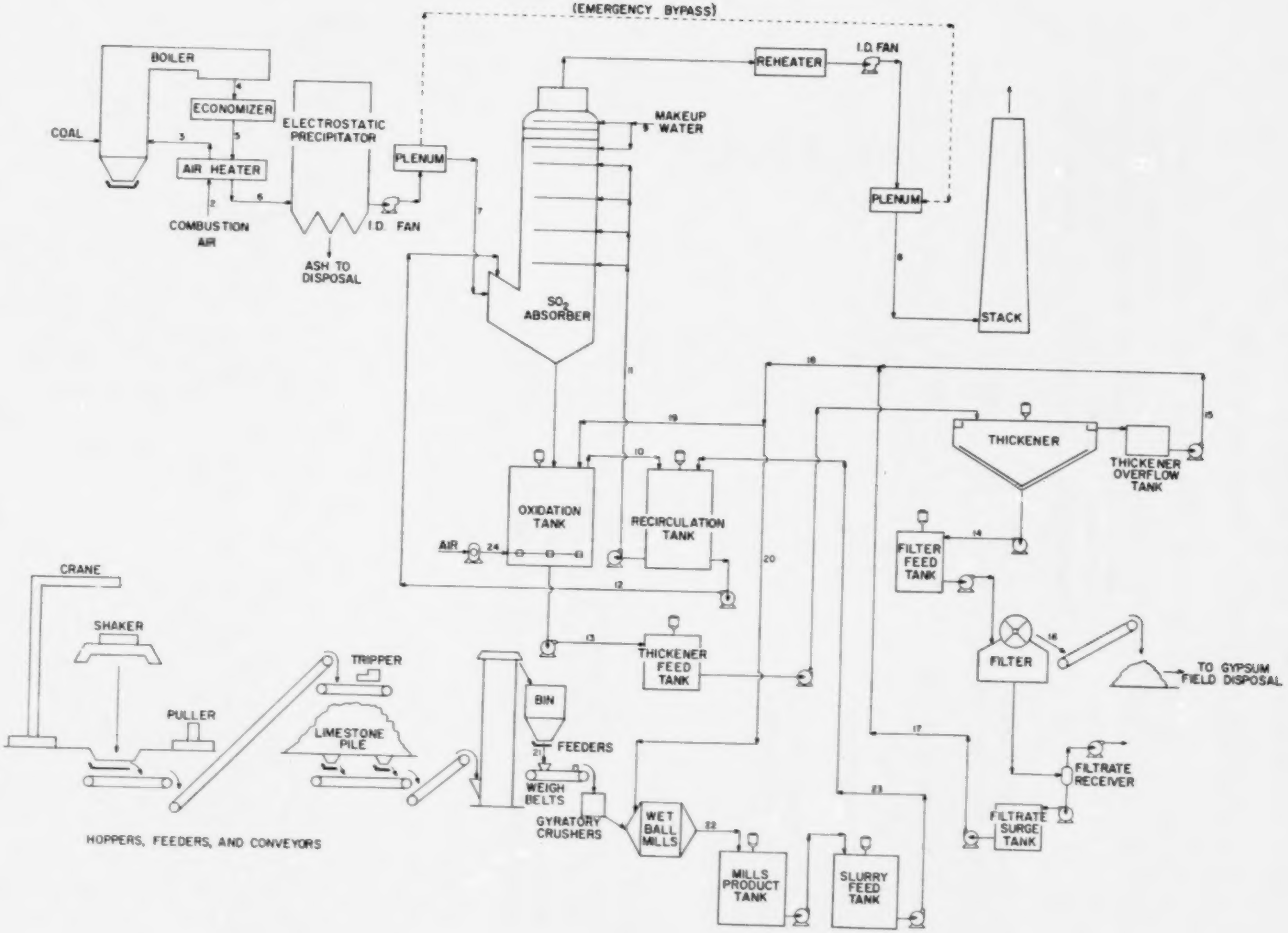


Figure 1. Base-case limestone process flow diagram.

The first two cases, no forced oxidation with ponding and forced oxidation with landfill, have the same absorber design conditions: $SO_2$ removal in the absorber to meet the revised 1979 NSPS, an L/G of 106, a limestone stoichiometry of 1.4, and no bypass (other than emergency bypass). The major difference is the forced oxidation, which increases sulfite oxidation from 30% to 95%. The absorber design conditions for the forced oxidation with adipic acid and landfill case are somewhat different from those for the first two cases. With the adipic acid enhancement (adipic acid concentration of 1,500 ppm) the $SO_2$ removal in the absorber is 95% at an L/G of 80 and a limestone stoichiometry of 1.07. With the higher $SO_2$ removal efficiency, partial flue gas bypass is used to reduce the reheat load.

Disposal Options--In the early 1970's ponding disposal was used or planned at 60% of the existing or planned utility FGD facilities. In 1980 ponding remained the primary disposal practice for operational units, but landfill was the dominant practice for units under construction and was almost solely planned for contracted units.

Pond--In the ponding case the waste slurry is removed from the effluent hold tank and pumped one mile to an onsite, clay-lined pond. After the waste solids settle out, the supernate is recycled to the effluent hold tank.

The disposal pond is a square, earthen-diked enclosure with a median diverter dike. The dikes are constructed from material removed from the impoundment area and the entire impoundment area is lined with 12 inches of clay (assumed available onsite). Pond size and depth are adjusted to minimize the land and construction costs.

Landfill--In the landfill cases the waste slurry from the oxidation tank is pumped to a thickener and then a filter. The thickener overflow and the filtrate are returned to the oxidation tank for reuse in the process. The filter cake is trucked to an onsite, clay-lined landfill.

The landfill is an area-type landfill having a square configuration with a single 20-foot lift and a 6-degree cap. After topsoil removal and storage, the landfill area is lined with 12 inches of clay (assumed available onsite) and 24 inches of bottom ash. The seepage through the landfill is collected and treated for pH adjustment (if necessary) before discharge. The landfill is surrounded by a catchment ditch which collects the rainfall runoff. The ditch drains into a catchment basin for control of suspended solids before discharge.

## Economic Premises

The limestone scrubbing economics consist of capital investments in mid-1982 dollars and first-year and levelized annual revenue requirements, both in mid-1984 dollars. The capital investments are based on major equipment costs developed from flow diagrams and material balances and factored costs for installation and ancillary equipment. First-year annual revenue requirements consist of raw material, operating, and overhead costs and levelized capital charges. In the levelized annual revenue requirements all costs are factored to account for a 10%/year discount rate and a 6%/year inflation rate for operating costs over the life of the power plant.

## RESULTS AND ECONOMIC COMPARISONS

In order to demonstrate the relative magnitude of the various costs which make up the total capital investment and the first-year and levelized annual revenue requirements for the limestone scrubbing process, the costs for three cases are given in more detail than the others, for which only the totals are shown. These three cases are conventional limestone process, the base-case limestone process, and the advanced limestone process. A 500-MW boiler burning a 3.5% sulfur coal is the assumed application for each case. The capital investments are shown in Table 4 and the first-year and levelized annual revenue requirements are shown in Table 5.

The conventional limestone process has a capital investment of $112.6M ($225/kW) in mid-1982 dollars. First-year and levelized annual revenue requirements are $28.8M (10.47 mills/kWh) and $39.4M (14.42 mills/kWh), respectively, in mid-1984 dollars.

The capital investment for the base-case limestone process is $103.1M ($206/kW). The first-year and levelized annual revenue requirements are $29.1M (10.58 mills/kWh) and $41.5M (15.08 mills/kWh) respectively.

The advanced limestone process has a capital investment of $92.8M ($186/kW) and first-year and levelized annual revenue requirements of $25.8M (9.38 mills/kWh) and $36.6M (13.31 mills/kWh) respectively.

The conventional limestone process has a higher (9.2%) capital investment than the base-case limestone process because of the higher capital investment required for the pond. The cost savings for the conventional limestone process in other investment areas including $SO_2$ scrubbing (no forced-oxidation equipment), solids separation (no thickener and filters), and landfill equipment (none required) are relatively minor.

The base-case limestone process costs are slightly higher than those previously reported by TVA (8) because they reflect recent modifications in the Shawnee lime/limestone computer model. These modifications include such major changes as revised spray tower design conditions and a revised landfill model, which account for most of the increase in costs, as well as minor changes such as hold tank residence times, thickener settling rates, slurry solids concentration, etc., which have little effect on costs.

The advanced limestone process has a lower (10.0%) capital investment than the base-case limestone process primarily because of the cost reductions in the $SO_2$ scrubbing area. Adipic acid enhances the absorption of $SO_2$ so that the L/G and limestone stoichiometry can be reduced, with a corresponding decrease in the costs for slurry recirculation pumps and piping. In addition, the use of adipic acid increases the $SO_2$ removal efficiency in the spray tower and allows partial scrubbing even for this high-sulfur coal case. Partial scrubbing decreases the size of the spray tower and also decreases the size of the inline-steam reheater since the 300°F bypassed gas is mixed with the scrubbed gas before entering the stack. The decrease in the limestone stoichiometry also reduces the costs for the raw material preparation, solids separation, and landfill areas, although these savings are relatively minor compared with those in the $SO_2$ scrubbing area.

## TABLE 4. CAPITAL INVESTMENT CONVENTIONAL, BASE-CASE, AND ADVANCED LIMESTONE PROCESSES

(500 MW, 3.5% sulfur in coal, revised 1979 NSPS, onsite waste disposal)

| | Capital investment, k$ | | |
|---|---|---|---|
| | Conventional limestone[a] | Base-case limestone[b] | Advanced limestone[c] |
| Direct Investment | | | |
| Raw material preparation | 7,244 | 7,244 | 6,848 |
| $SO_2$ scrubbing | 35,281 | 37,872 | 33,770 |
| Solids separation | 2,646 | 3,679 | 3,456 |
| Total process capital | 45,172 | 48,795 | 44,074 |
| Services, utilities, and miscellaneous | 2,710 | 2,928 | 2,645 |
| Total direct (excluding waste disposal) | 47,882 | 51,723 | 46,719 |
| Landfill equipment | - | 1,046 | 830 |
| Landfill or pond construction | 15,296 | 3,858 | 3,422 |
| Total direct investment | 63,178 | 56,627 | 50,971 |
| Indirect Investment | | | |
| Engineering design and supervision | 3,352 | 3,621 | 3,270 |
| Architect and engineering contractor | 958 | 1,034 | 934 |
| Construction expense | 7,661 | 8,275 | 7,475 |
| Contractor fees | 2,394 | 2,586 | 2,336 |
| Contingency | 6,225 | 6,724 | 6,073 |
| Waste disposal indirects | 4,222 | 1,707 | 1,496 |
| Total fixed investment | 87,989 | 80,574 | 72,555 |
| Other Capital Investment | | | |
| Allowance for startup and modification | 5,478 | 5,917 | 5,345 |
| Interest during construction | 13,726 | 12,570 | 11,319 |
| Royalties | - | - | - |
| Land | 1,986 | 614 | 548 |
| Working capital | 3,376 | 3,392 | 3,003 |
| Total capital investment | 112,552 | 103,067 | 92,770 |
| $/kW | 225 | 206 | 186 |

Basis: Upper midwest plant location represents project beginning mid-1980, ending mid-1983. Average cost basis, mid-1982. Spare pumps, scrubbing train, and feed preparation train. Disposal pond and landfill located one mile from plant. Investment includes FGD feed plenum but excludes stack plenum and stack.

a. Spray tower, no forced-oxidation, pond.
b. Spray tower, forced-oxidation, landfill.
c. Spray tower, forced-oxidation, adipic acid, landfill.

## TABLE 5. ANNUAL REVENUE REQUIREMENTS CONVENTIONAL, BASE-CASE, AND ADVANCED LIMESTONE PROCESSES

(500 MW, 3.5% sulfur in coal, revised 1979 NSPS,
onsite waste disposal)

| | Total annual cost, k$ | | |
|---|---|---|---|
| | Conventional limestone[a] | Base-case limestone[b] | Advanced limestone[c] |
| **Direct Costs** | | | |
| Raw material | | | |
| Limestone | 1,214 | 1,214 | 927 |
| Adipic acid | - | - | 208 |
| Subtotal raw material | 1,214 | 1,214 | 1,135 |
| **Conversion Costs** | | | |
| FGD operating labor and supervision | 460 | 658 | 644 |
| Landfill operating labor and supervision | - | 612 | 524 |
| Utilities | | | |
| Steam | 1,356 | 1,355 | 1,063 |
| Process water | 38 | 27 | 25 |
| Electricity | 1,873 | 2,133 | 1,666 |
| Diesel fuel | - | 165 | 117 |
| Maintenance | 4,290 | 4,285 | 3,865 |
| Analyses | 104 | 105 | 70 |
| Subtotal conversion costs | 8,121 | 9,340 | 7,974 |
| Subtotal direct costs | 9,335 | 10,554 | 9,109 |
| **Indirect Costs** | | | |
| Overheads, plant and administrative | 2,912 | 3,395 | 3,062 |
| Total first-year operating and maintenance costs | 12,247 | 13,949 | 12,171 |
| Levelized capital charges | 16,545 | 15,151 | 13,637 |
| Total first-year annual revenue requirements | 28,792 | 29,100 | 25,808 |
| Equivalent first-year unit revenue requirements, mills/kWh | 10.47 | 10.58 | 9.38 |
| Levelized total operating and maintenance costs | 23,097 | 26,309 | 22,954 |
| Levelized capital charges | 16,545 | 15,151 | 13,637 |
| Total levelized annual revenue requirements | 39,642 | 41,460 | 36,591 |
| Equivalent levelized unit revenue requirements, mills/kWh | 14.42 | 15.08 | 13.31 |

Basis: Upper midwest plant location, mid-1984 revenue requirements. New plant with 30-year life and on-stream time of 5,500 hr/yr.

a. Spray tower, no forced-oxidation, pond.
b. Spray tower, forced-oxidation, landfill.
c. Spray tower, forced-oxidation, adipic acid, landfill.

The advanced limestone process has the lowest annual revenue requirements and the base-case limestone process has the highest. The raw material costs are essentially the same for all three cases. The largest differences are in the levelized capital charges, which are calculated as a percentage of the total capital investment. The base-case limestone process has the highest annual revenue requirements because of the higher landfill labor (the ponding case has no labor associated with pumping of the slurry to the pond), electricity, diesel fuel, and overhead costs.

## Sensitivity of Economic Results to Design Changes

Although the base-case limestone process as described in this paper represents the type of process the industry is turning toward, there are many systems operating, under construction, or being planned that incorporate other designs. Thus various design changes were simulated using the computer model to show the effect of these changes on the limestone scrubbing economics. The design changes simulated are: boiler size and coal sulfur level, type of absorber, type of waste disposal, absorber design conditions (for the spray tower case only), and the use of additives.

### Power Unit Size and Coal Sulfur Level--

The effect of power unit size (200 MW, 500 MW, and 1,000 MW) and different coal sulfur levels (2.0% S, 3.5% S, and 5.0% S) on capital investment and unit revenue requirements is shown in Table 6 and in Figure 2. The usual economy of scale effect in terms of unit costs ($/kW, mills/kWh) is evident for all conditions. For a given coal sulfur level the capital investments of 500-MW cases are about 33% less expensive in terms of $/kW, than the 200-MW cases and the 1,000-MW cases are about 13% less expensive than the 500-MW cases. First-year annual revenue requirements, in mills/kWh, for a 500-MW unit at a given coal sulfur level are about 33% less expensive than the 200-MW cases while the 1,000-MW cases are about 15% less expensive than the 500-MW cases. Similar cost relativities are obtained for similar variations in the conventional and advanced processes.

### Type of Absorber--

The base-case FGD application (500 MW, 3.5% S coal, forced oxidation, landfill) was used to evaluate the cost difference between limestone scrubbing processes using three types of absorbers (TCA, spray tower, and venturi - spray tower). The design conditions for the three absorbers were previously shown in Table 2. The TCA-based limestone process has the lowest capital investment and the venturi - spray tower process has the highest, as shown in Table 7. The major capital investment advantage of the TCA-based process lies in the lower costs for the $SO_2$ absorption area because of the smaller absorber (the TCA operates at a higher superficial gas velocity). Other contributions to the lower capital investment in the $SO_2$ absorption area for the TCA are the smaller pumps because of the lower L/G required. The capital investment for the reheat area is also slightly lower because of the higher pressure drop in the TCA, and subsequently higher heat of compression through the ID fan.

The process using the larger spray tower at a lower pressure drop has a higher capital investment for the $SO_2$ absorption and reheat areas than the

## TABLE 6. ECONOMICS OF THE BASE-CASE LIMESTONE PROCESS AS A FUNCTION OF POWER UNIT SIZE AND COAL SULFUR LEVEL[a]

(Spray tower, forced oxidation, landfill)

| Power unit size, MW | Sulfur in coal, % 2.0 | 3.5 | 5.0 |
|---|---|---|---|
| Capital Investment, $/kW | | | |
| 200 | 267.2 | 295.3 | 312.9 |
| 500 | 177.1 | 206.1 | 218.3 |
| 1,000 | 155.5 | 177.2 | 187.0 |
| First-Year Annual Revenue Requirements, mills/kWh | | | |
| 200 | 13.58 | 15.21 | 16.17 |
| 500 | 8.85 | 10.58 | 11.36 |
| 1,000 | 7.55 | 8.97 | 9.63 |
| Levelized Annual Revenue Requirements, mills/kWh | | | |
| 200 | 19.29 | 21.69 | 23.08 |
| 500 | 12.51 | 15.08 | 16.25 |
| 1,000 | 10.59 | 12.71 | 13.73 |

a. Based on TVA Design and Economic Premises.

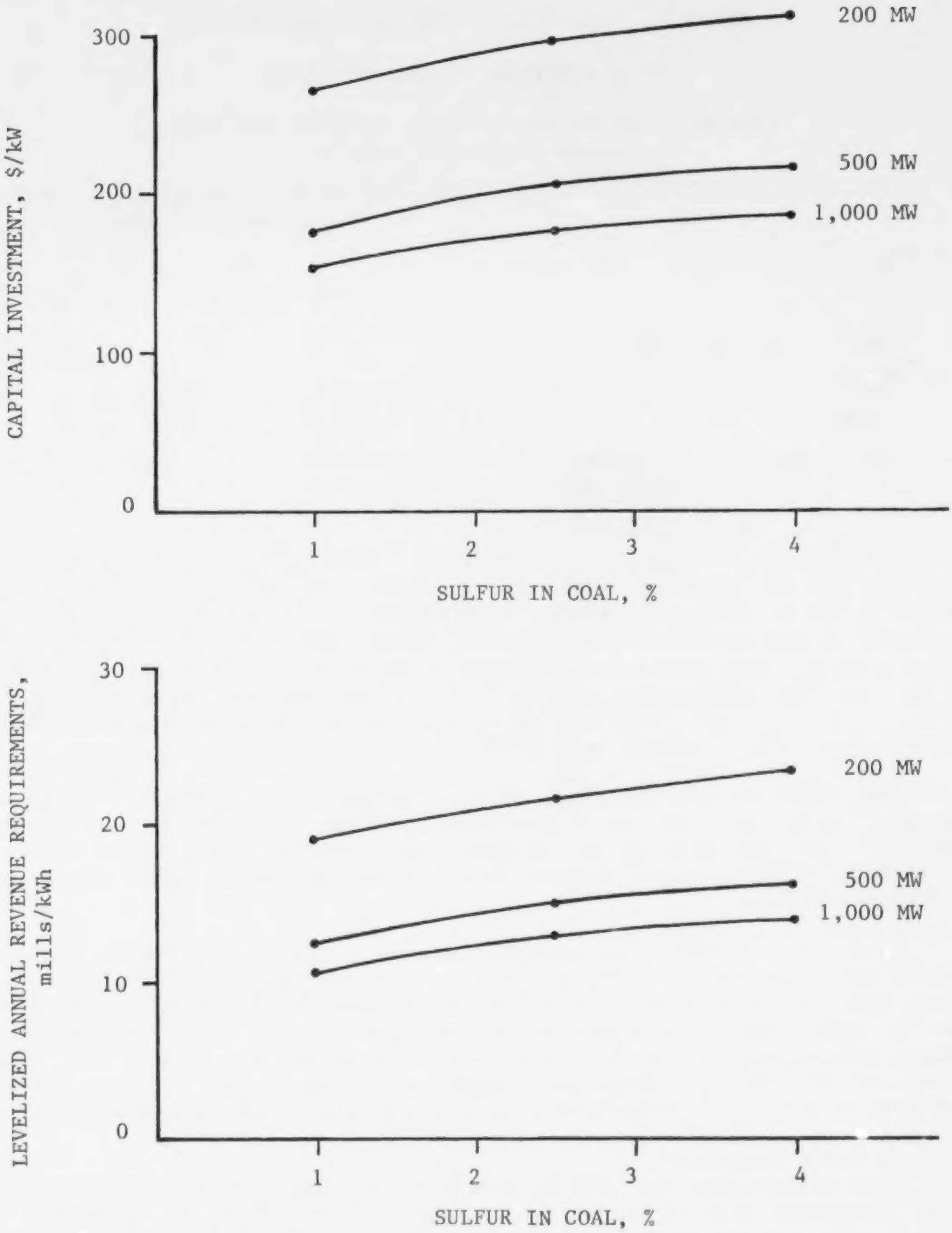


Figure 2. Economics of the base-case limestone process as a function of power unit size and coal sulfur level.

### TABLE 7. ECONOMICS OF THE LIMESTONE PROCESS AS A FUNCTION OF ABSORBER TYPE[a]

(500 MW, 3.5% sulfur in coal, revised 1979 NSPS,
forced oxidation, landfill)

| | Absorber type | | |
|---|---|---|---|
| | TCA | Spray tower | Venturi - spray tower |
| Capital investment, $/kW | 197 | 206 | 218 |
| Annual revenue requirements, mills/kWh | | | |
| First year | 10.09 | 10.58 | 11.20 |
| Levelized | 14.37 | 15.08 | 15.96 |

a. Based on TVA Design and Economic Premises.

TCA-based process. This is only partially offset by the lower capital investment in the gas handling area. The process using the venturi - spray tower absorber has a higher limestone utilization rate, and thus slightly lower capital investments for the feed preparation, dewatering, and disposal areas. This is more than offset by the higher capital investments for the gas handling and $SO_2$ absorption areas, however, making the process using this absorber combination somewhat higher in capital investment than processes using a TCA (11%) or spray tower (6%).

The same cost relationships (i.e., TCA lowest and venturi - spray tower highest) also prevail in the annual revenue requirements as shown in Table 7. The differences are largely the result of costs based on capital investment such as capital charges and maintenance. Other annual costs do not differ greatly.

Although the TCA-based process appears to have the lowest costs, it should be noted that the current trend in the utility industry is to the spray tower absorber because of its simplicity and more trouble-free operation. The use in this study of factored estimates based on the capital investment for annual maintenance costs does not allow for field experience with various types of absorbers. Thus the annual maintenance cost for the TCA-based process is probably underestimated relative to the spray tower-based process.

Type of Waste Disposal--

Cost comparisons for 500-MW conventional limestone (ponding) and base-case limestone (forced-oxidation - landfill) processes at different coal sulfur contents are shown in Figure 3. In all cases the capital investment for the conventional limestone process is higher and the difference increases with increasing coal sulfur content. These higher capital investments are largely the result of the disposal area construction costs, which are typi-

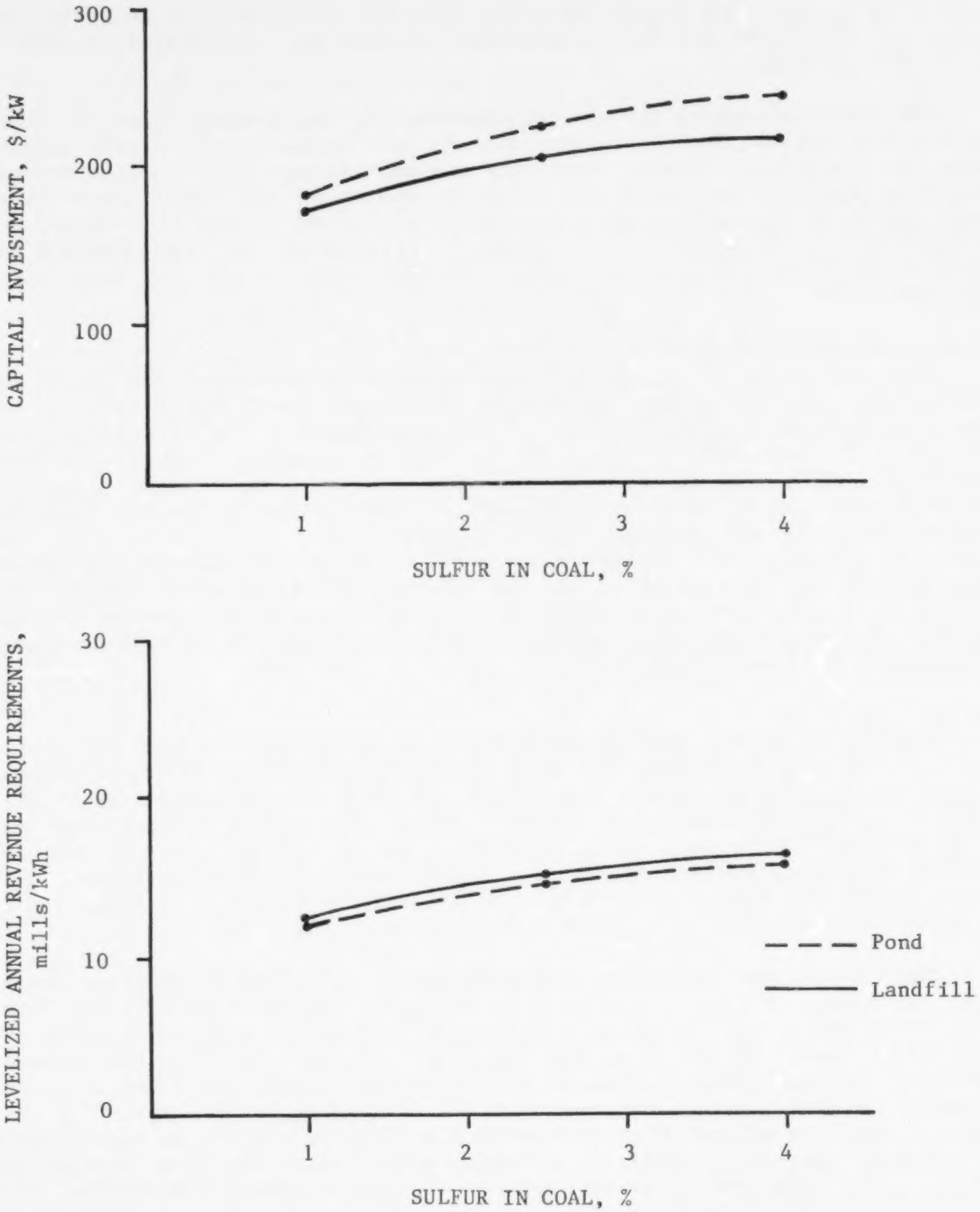


Figure 3. Economics of the limestone process as a function of coal sulfur level and waste disposal type.

cally five to six times higher for ponds than for landfills. In contrast, the additional investment for forced oxidation, dewatering, and landfill equipment is relatively small.

The levelized annual revenue requirements for the ponding cases are lower for all coal cases. The lower operating and maintenance costs for the ponding cases are the primary cause. Operating and maintenance costs for the forced-oxidation landfill processes are slightly higher in all cases where these costs are more than offset by the savings in capital charges. However, the differences in levelized annual revenue requirements for the ponding and landfill cases are relatively insignificant when compared with the total costs involved.

### Absorber Design Conditions--

Once the superficial gas velocity through the absorber, the pH of the slurry, and the $SO_2$ removal efficiency have been specified, either of the remaining absorber design criteria, L/G or stoichiometry, can be specified and the other is calculated. Thus it becomes an economic trade-off between increasing cost for electricity for the slurry recirculation pumps or increasing the annual cost for limestone and the investment for the limestone preparation equipment and the waste disposal area. As can be seen from Figure 4, increasing the stoichiometry and decreasing the absorber L/G is the most economically attractive of the two options for the landfill cases. This analysis does not, however, consider the increased operability and reliability problems due to scaling and plugging that may be encountered at high limestone stoichiometries (i.e., above 1.4).

### Use of Additives--

The use of adipic acid as an additive to enhance the efficiency of the limestone scrubbing process has shown that it can help existing limestone systems achieve significant improvement in $SO_2$ removal efficiency (9). However, questions have been raised about its attractiveness for new installations where a well-designed FGD system can achieve the required $SO_2$ removal efficiency without resorting to additives. In addition dibasic acid (DBA), which is a byproduct of adipic acid manufacture, has been suggested as an alternative to adipic acid because of its lower unit cost.

Table 8 compares the relative process economics of three limestone scrubbing processes. All are based on a spray tower, forced-oxidation, and landfill system for a new 500-MW unit burning a 3.5% sulfur coal and meeting the 1979 NSPS. Case 1 is the base-case limestone process, case 2 is the advanced limestone process (which is enhanced with adipic acid), and case 3 is the advanced limestone process enhanced with DBA instead of adipic acid. For this case, it has been assumed that the use of dibasic acid results in improvements in scrubber operation identical to improvements resulting from the use of adipic acid. The DBA, however, appears to have a higher degradation rate (approximately 1/3 higher) than adipic acid and thus the DBA addition rate is higher in order to maintain the same additive concentration in the scrubbing slurry (9). More test work needs to be done with DBA to confirm these design assumptions, particularly since DBA-enhancement has never been tested in the forced-oxidation mode.

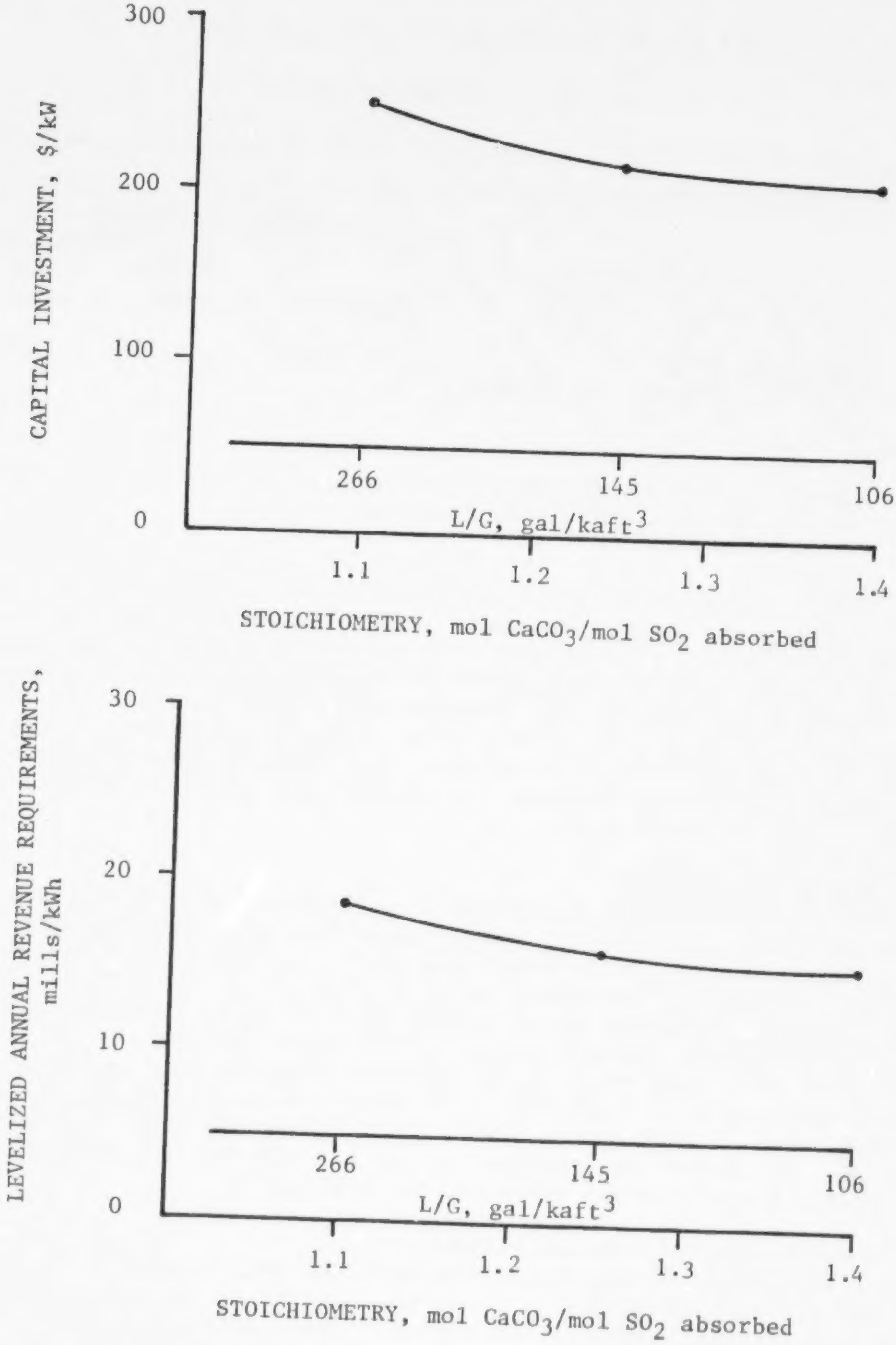


Figure 4. Economics of the base-case limestone process as a function of absorber stoichiometry.

TABLE 8. ECONOMICS FOR THE BASE-CASE AND

THE ADVANCED LIMESTONE PROCESS[a]

(500 MW, 3.5% sulfur in coal, revised 1979 NSPS, onsite waste disposal)

| | Limestone process | | |
|---|---|---|---|
| | | Advanced | |
| | Base-Case | Adipic acid | Dibasic acid |
| Capital investment, $/kW | 206 | 186 | 186 |
| Annual revenue requirements, mills/kWh | | | |
| First year | 10.58 | 9.38 | 9.35 |
| Levelized | 15.08 | 13.31 | 13.25 |

a. Based on TVA Design and Economic Premises.

The capital investments for the acid-enhanced, advanced limestone processes are about 10% lower than that for the base-case limestone process ($186/kW versus $206/kW respectively). The first-year annual revenue requirements are 11% lower for the acid-enhanced, advanced limestone processes. In terms of levelized annual revenue requirements, the acid-enhanced, advanced limestone processes also are lower. The use of the less expensive DBA ($640/ton, dry basis) instead of adipic acid ($1,500/ton, dry basis) has essentially no effect on capital investment and reduces annual revenue requirements only insignificantly.

Effect of Adipic Acid Cost--

For the advanced limestone process a delivered cost for adipic acid of $1,500/ton was used. Since adipic acid is made from petroleum and thus may be subject to rapid increases in delivered cost, a sensitivity analysis was performed to demonstrate the effect of ±20% changes in the delivered cost of adipic acid on the economics of an adipic acid-enhanced, advanced limestone process. The resulting process economics are shown in Table 9. The capital investment and the first-year annual revenue requirements are essentially constant, increasing only 0.05% and 0.2% respectively for a 20% increase in the delivered cost of adipic acid. Thus, although adipic acid is an expensive raw material, the annual consumption is low and the cost is negligible when compared with the other annual costs for the FGD system.

Effect of Adipic Acid Degradation Factor--

Adipic acid tends to degrade in the absorber into a mixture of primarily valeric and glutaric acids but with lesser amounts of butyric and succinic acids, carbon dioxide, methane, and butane. Some adipic acid will also be lost with the waste going to the landfill. In order to simplify the model, adipic acid losses due to degradation and to the landfill are lumped together as a single degradation factor. For the advanced limestone process as

### TABLE 9. SENSITIVITY ANALYSES FOR THE ADVANCED LIMESTONE PROCESS[a]

(500 MW, 3.5% sulfur in coal, revised 1979 NSPS, onsite waste disposal)

| | Advanced limestone process | | | | | | |
|---|---|---|---|---|---|---|---|
| | Adipic acid cost, $/ton | | | Adipic acid degradation factor | | | Worst case: Cost of $1,800/ton and degradation factor of 9 |
| | 1,200 | 1,500[b] | 1,800 | 3[b] | 6 | 9 | |
| Capital investment, $/kW | 185.5 | 185.5 | 185.6 | 185.5 | 185.6 | 185.7 | 185.8 |
| Annual revenue requirements, mills/kWh | | | | | | | |
| First year | 9.37 | 9.38 | 9.40 | 9.38 | 9.46 | 9.54 | 9.59 |
| Levelized | 13.28 | 13.31 | 13.33 | 13.31 | 13.45 | 13.60 | 13.69 |

a. Based on TVA Design and Economic Premises.
b. Base-case conditions.

discussed in this paper, the makeup adipic acid rate to replace adipic acid lost by degradation and to the landfill is assumed to be three times the rate of adipic acid loss to the landfill. Therefore the advanced limestone process is said to have a degradation factor of 3.

However, adipic acid use in full-scale limestone FGD systems is relatively new and sufficient data are currently not available to predict adipic acid losses accurately for specific cases. Therefore a sensitivity analysis was performed to illustrate the change in process economics as the adipic acid-degradation factor is increased threefold (from an initial value of 3 to a worst case value of 9). The results are shown in Table 9. Doubling the adipic acid-degradation factor increases the capital investment less than 0.06% and increases the first-year annual revenue requirements by only about 0.9%. Tripling the degradation factor increases the capital investment about 0.1% and increases the first-year annual revenue requirements by only about 1.7%. Thus the annual consumption even at high degradation rates results in a negligible increase in process costs.

### Combined Effect of Adipic Acid Cost and Degradation Factor--

A worst case example was prepared in which both the highest unit cost and the highest degradation factor for adipic acid were used. As shown in Table 9 even in this worst case the capital investment increases only 0.2% and the first-year annual revenue requirements increase only 2.2%. Thus, within reasonable limits, the delivered cost for adipic acid and the degradation factor have essentially no effect on the process economics.

## CONCLUSIONS

From the economic summary data presented in this paper, several conclusions about the various limestone scrubbing options can be made.

- Processes with forced oxidation and landfill disposal have lower capital investments than pond disposal processes, but slightly higher first-year and levelized annual revenue requirements for most coal applications.

- The use of adipic acid or DBA to enhance $SO_2$ removal is an effective method of reducing overall costs. The capital investment for the enhanced-limestone processes is approximately 10% lower than those for the base-case limestone process and about 11% lower in terms of annual revenue requirements. Based on the design assumptions made concerning DBA addition, the cost savings achieved by using DBA instead of adipic acid are marginal.

- The cost of adipic acid is a negligible component of the annual revenue requirements for the advanced limestone process and therefore significant changes in either the cost or the degradation rate result in negligible changes in the overall process economics.

- Of the two absorber design conditions that are normally specified by the designer, stoichiometry and L/G, for a forced-oxidation, landfill case it is more cost effective to minimize the absorber L/G while increasing stoichiometry.

- The TCA-based limestone process excluding disposal cost has the lowest capital investment and annual revenue requirements of the three absorber types. The venturi - spray tower-based process has the highest. [It should be noted that although the TCA-based process appears to have the lowest costs, the current trend in the utility industry is to the spray tower absorber because of its simplicity and more trouble-free operation.]

## DISCLAIMER

This paper was prepared by the Tennessee Valley Authority and has been approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Tennessee Valley Authority or the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

## ACKNOWLEDGMENTS

This study was funded by the Environmental Protection Agency through EPA/TRA Interagency Agreement No. 79-DX-0511. EPA project officers for this study are J. D. Mobley and C. C. Masser.

## REFERENCES

1. D. A. Burbank and S. C. Wang, 1980, EPA Alkali Scrubbing Test Facility: Advanced Program - Final Report (October 1974-June 1978), EPA-600/7-80-115, U.S. Environmental Protection Agency, Washington, D.C.

2. W. L. Anders and R. L. Torstrick, 1981, Computerized Shawnee Lime/Limestone Scrubbing Model Users Manual, EPA-600/8-81-008, U.S. Environmental Protection Agency, Washington, D.C.

3. J. D. Hatfield, Y. K. Kim, and R. C. Mullins, 1972, Sulfur Oxide Removal from Power Plant Stack Gas - Study of the Effect of Organic Acids on the Wet-Limestone Scrubbing Process, TVA Special Report No. 458, prepared for EPA under contract No. TV-34425A, February 24, 1972.

4. G. T. Rochelle, 1977, Process Synthesis and Innovation in Flue Gas Desulfurization, Ph. D. Disseration, University of California at Berkeley.

5. G. T. Rochelle and C. J. King, 1977, The Effect of Additives on Mass Transfer in $CaCO_3$ or CaO Slurry Scrubbing of $SO_2$ from Waste Gases, Industrial and Engineering Chemistry, Fundamental, Vol. 16, No. 1, pp. 67-75.

6. H. N. Head, S. C. Wang, D. T. Rabb, R. H. Borgwardt, J. E. Williams, and M. A. Maxwell, 1979, Recent Results from EPA's Lime/Limestone Scrubbing Programs - Adipic Acid as a Scrubber Additive, In: Proceedings: Symposium on Flue Gas Desulfurization - Las Vegas, Nevada, March 1979, Vol. 1, EPA-600/7-79-167a, U.S. Environmental Protection Agency, Washington, D.C., pp. 342-385.

7. D. A. Burbank, S. C. Wang, R. R. McKinsey, and J. E. Williams, 1980, Test Results on Adipic Acid - Enhanced Limestone Scrubbing at the EPA Shawnee Test Facility - Third Report - preprint of paper presented at the Sixth EPA Symposium on Flue Gas Desulfurization, Houston, Texas, October 28-31, 1980.

8. G. G. McGlamery, W. E. O'Brien, C. D. Stephenson, and J. D. Veitch, 1980, FGD Economics in 1980, In: Proceedings: Symposium on Flue Gas Desulfurization - Houston, Texas, October 1980, Vol. 1, EPA-600/9-81-019a, U.S. Environmental Protection Agency, Washington, D.C., pp. 49-84.

9. O. W. Hargrove, Jr., J. D. Colley, and J. D. Mobley, 1981, Adipic-Acid-Enhanced Limestone Flue Gas Desulfurization System Commercial Demonstration, Paper presented at the APCA/ASME Environmental Information Exchange, Research Triangle Park, North Carolina, December 8-9, 1981.

# Session 2: MATERIALS OF CONSTRUCTION

Charles E. Dene, Chairman
Electric Power Research Institute
Palo Alto, CA

# MATERIALS PROBLEM: OPERATING A CLOSED-LOOP LIMESTONE FGD SYSTEM

by: Daniel A. Froelich, P.E.
Manager, Air Quality Design Department
Burns & McDonnell Engineering Co.
P.O. Box 173
Kansas City, Missouri 64141

and

Marcus W. Ware, P.E.
Manager of Production
South Mississippi Electric
Power Association
P.O. Box 1589
Hattiesburg, Mississippi 39401

## ABSTRACT

The wet limestone closed-loop sulfur dioxide absorption systems for both units of the R.D. Morrow, Sr. Generating Plant have experienced significant failure in their corrosion-protection measures. Initial corrosive attack was evident in the absorber module and the inlet and outlet ductwork through the stack breeching. After inspector and supplier analyses, rubber lining replaced the protective polyester coating in the absorber module. HASTELLOY alloy G replaced the coatings in the ductwork. After operations had been resumed for a few months, the rubber lining appeared satisfactory. The alloy G, however, was showing signs of failure, especially in the mixing zone and the stack breeching. Further testing and analysis were performed. Attention was turned to HASTELLOY alloy C-276. This alloy had been a corrosion-resistor as a weld material for the alloy G cladding. It was decided to reclad selected areas of the ductwork and absorber inlet nozzle with alloy C-276. After a short period of operation, some of these areas also exhibited corrosive attack. Because of the alloy problems, various coatings were considered and installed over those areas of HASTELLOY alloy G showing the worst corrosive attack. This coatings program found that an epoxy and some of the fluoroelastomers provided some substantive protection. Further coatings testing is underway in a program sponsored by EPRI. This program will also evaluate again selected alloys.

# INTRODUCTION

Of all of the problems that could beset a flue gas desulfurization (FGD) system, the one that most challenges system designers, manufacturers, and users alike is corrosion. The environment within an FGD system is a complex interface of solids, liquids, and gases which is characterized by critical temperature fluctuations and unknown chemical reactions. This activity is bound to take its toll on the inner surfaces of ductwork, dampers, piping, pumps, and other vessels. Much of this activity is mitigated when the system can constantly purge itself of these fluid-solid compounds. Such is the benefit of an open-loop FGD system.

A closed-loop FGD system is another matter. By eliminating any water discharges from the $SO_2$ absorption system, except for that minimal amount of water leaving with the sludge, various corrosive salts are concentrated within the absorption loop. The corrosive compounds reach equilibrium such that the ions entering equal those leaving the system through the water in the sludge. This results in very high levels of certain ion species within the closed-loop system. These compounds appear to be the primary cause of corrosion.

The R. D. Morrow plant has one of the first limestone FGD systems to be operated continuously in a truly closed-loop mode. During the absorber characterization testing, chlorides within the plant's absorption loop built up to or exceeded a level of 15,000 ppm.

Both the operation of the closed-loop system and the materials of construction used in the FGD system have been a major concern to the designer, the manufacturer, and the utility. As will be demonstrated in this case history, engineering judgement faced a sizable challenge. The end result is still to be realized. But all concerned with the plant as well as the industry as a whole have profited from some of the lessons learned so far.

The paper is broken into the following divisions.

1. Plant Parameters.
2. FGD System Design and History.
    a. Coatings.
    b. HASTELLOY® alloy G.
    c. HASTELLOY alloy C-276.
    d. Coatings - Reevaluation.
    e. Current Plans.
3. Summary and Conclusions.

Some effort has been made to present activities in a reasonably chronological order. Overlapping, however, does occur.

---

HASTELLOY® is a registered trademark of the Cabot Corporation.

## PLANT PARAMETERS

The R. D. Morrow, Sr. Generating Station consists of two duplicate units each having a nameplate capacity of 203 MW with a net capacity of 180 MW. Unit 1 went commercial April 16, 1978, while Unit 2 went commercial December 1, 1978. Due to the time frame on the initial design, both these units were designed to meet the 1971 New Source Performance Standards. The standards limited the particulate emissions to 43 ng/J (0.1 lbs/MBtu), the sulfur dioxide to 520 ng/J (1.2 lbs/MBtu), and the nitrogen oxides to 300 ng/J (0.7 lbs/MBtu).

The fuel comes from a Kentucky coal property owned by the utility. A preparation plant at the mine cleans the coal before shipment to the Morrow site. This coal has an average chlorine concentration of 0.1 percent and a sulfur content of 1.23 percent with a higher heating value of 12,600 Btu/lb (see Table 1). The fluoride concentration averages 0.01 percent by weight.

TABLE 1. COAL ANALYSIS*

| Parameter | Average | Range |
|---|---|---|
| Moisture, % | 4.18 | 2.26 - 5.40 |
| Carbon, % | 70.80 | 69.57 - 71.87 |
| Hydrogen, % | 4.81 | 4.72 - 4.88 |
| Nitrogen, % | 1.19 | 1.05 - 1.44 |
| Chlorine, % | .10 | 0.06 - 0.12 |
| Sulphur, % | 1.23 | 1.15 - 1.36 |
| Ash, % | 10.68 | 9.99 - 12.63 |
| Oxygen (diff.), % | 7.0 | 6.58 - 7.74 |
| HHV, Btu/lb | 12,637 | 12,576 - 12,783 |

---

* Average value and ranges determined from four fired coal analyses sampled during the 60 day chemical characterization testing.

Due to its proximity to a pristine river, the overall water balance for the total power plant was reviewed very carefully by the regulatory agencies. Basically, the quantity of water leaving the plant site had to be minimized. Very strict quality requirements were placed on the discharge water. The only two waste streams allowed to leave the plant site are cooling tower blowdown and neutralized coal-pile runoff. To meet these requirements, the gas-cleaning system was designed for a closed-loop operation (Figure 1) so that the final waste could be disposed of in a landfill located on the plant site. Makeup for the $SO_2$ absorption system comes from demineralizer regeneration waste, treated sanitary wastes, boiler blowdown, and floor drains. If additional water is required, blowdown from the cooling tower system is used.

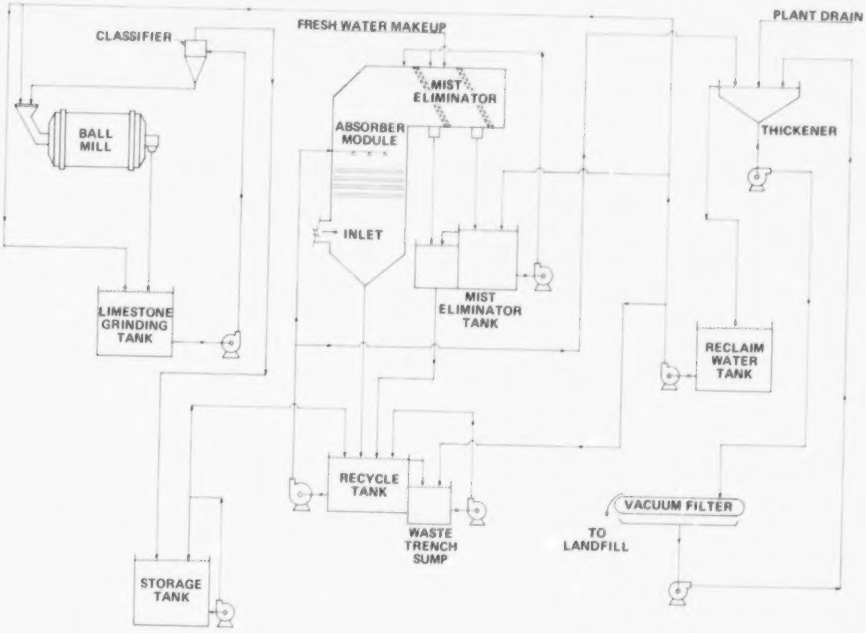


Figure 1. Absorption System Water Balance

The gas-cleaning system for the Morrow Plant consists of a hot-side precipitator for particulate control and a limestone absorption system for sulfur dioxide control. The boiler was designed to control nitrogen oxide emissions.

## FGD SYSTEM DESIGN AND HISTORY

Since most of the corrosion problems at the Morrow Plant stem from the FGD system, this system will be examined in more detail.

The FGD system specifications were written during the latter part of 1974 with the contract awarded in May of 1975. The contract was for a rod absorber which is, basically, a vertical tower with stages of 316 stainless-steel rod decks which provide surface for mass transfer. A two-pass horizontal mist eliminator was supplied to remove entrained slurry. Unit 1's FGD system went on line September of 1978 with full-load operation achieved one month later. The design gas flow for each unit was 686,477 cubic meters per hour at 51.7 degrees C (404,000 acfm at 125 degrees F). A critical design parameter was that the FGD system treat only 60 percent of the flue gas. This minimized the absorption system's capital cost and allowed 40 percent of the flue gas to be bypassed for reheat purposes.

The initial design of the corrosion protection system for the FGD system consisted of several linings of various materials. Below the lowest rod deck of the absorbers, the walls and absorber floor were lined with brick attached to the vessel with an asphaltic coating. This material was removed during the first few months of operation because it did not prove to be structurally sound. The inlet portion of the absorbers, the interior of the absorber, the absorber outlet ductwork, the mixing chamber ductwork, and the ductwork from the mixing chamber to the stack were all protected by a glass-flake-filled polyester coating.

In the mixing zone area, where the bypass and scrubbed gases interface, a set of fiberglass tubes was provided as a mixing device (Figure 2). These tubes were supported by a sheet of alloy G material and all bracing between the tubes was fabricated of alloy G. On Unit 1 the mixing tubes were removed and reinstalled during the cladding of the ductwork with alloy G. During cladding work on Unit 2 with HASTELLOY alloy G, the mixing tubes were removed from the mixing duct and not reinstalled because they showed signs of delamination. After three months of operation Unit 1's mixing tubes were removed. Inspections after initial operation indicated sufficient mixing could be achieved without the tubes.

The sludge treatment system consists of a thickener which dewaters the 15 percent solids slurry to approximately 40 percent solids; next follows a vacuum filter which dewaters the sludge from approximately 40 percent to 70 percent or possibly even more depending on the level of calcium sulfate in the scrubber sludge; and then lastly, a pug mill where the sludge from the vacuum filter is mixed with dry fly ash and ultimately disposed of in a landfill. All water that is removed from the sludge is returned to the FGD system to be used as makeup water to the ball mills or as makeup to the mist eliminator wash system.

## COATINGS

Full-load operation on the gas cleaning system was achieved in October

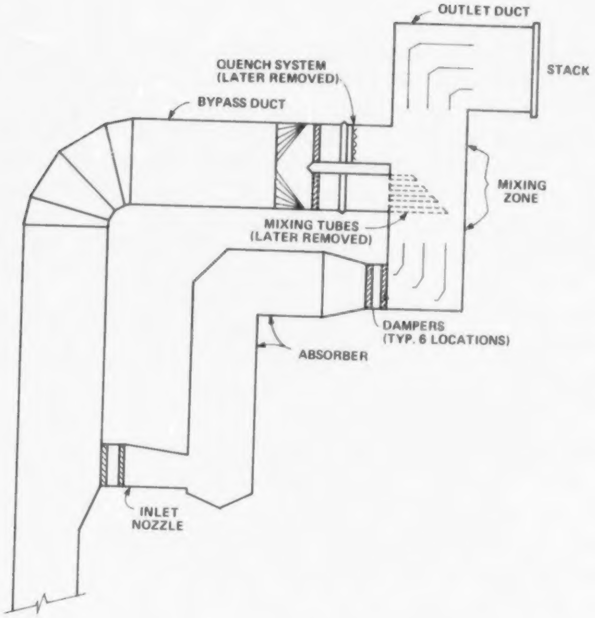

OUTLET DUCT
STACK
QUENCH SYSTEM (LATER REMOVED)
BYPASS DUCT
MIXING ZONE
MIXING TUBES (LATER REMOVED)
DAMPERS (TYP. 6 LOCATIONS)
ABSORBER
INLET NOZZLE

Figure 2. $SO_2$ Absorption System Ductwork Arrangement

1978. The unit operated through December at which time an inspection revealed failure of the coatings in both the hold tank and the ductwork. The flake-glass polyester coating supplier indicated that the failures in these areas were due to application problems and the ductwork and tank were recoated with the same material.

In March 1979, after approximately two months of operation, the reapplied coating in the ductwork also failed. At that time several different coating suppliers were contacted to find out if a guarantee would be offered for the coating materials. One of the suppliers offered a guarantee for his flake glass polyester coating but he limited the flue gas temperature in this outlet ductwork to 93.3 degrees C (200 degrees F). This supplier's offer was accepted. However, modifications had to be made to the system to meet the temperature limitation. The absorber manufacturer designed a bypass quench system which was installed in the bypass duct at the same point where the coating starts (Figure 2), intending to limit the temperatures to 93.3 degrees C when the unit was on bypass. The quench system was not required when the absorbers were on line because the final mix temperature of bypass and scrubbed gas was below 93.3 degrees C. With the coating applied, after several weeks of initial operation the ductwork in the general vicinity of the quenching sprays exhibited some failure of the coating. It was decided that in this interface area a seven-foot band of cladding of HASTELLOY alloy G be installed to minimize the corrosion effects of the quench spray on the ductwork itself.

## HASTELLOY ALLOY G

By July 1979, corrosion and erosion problems in both the gas cleaning system and outlet ductwork were severe. A review was made of all materials of construction. Part of the review included an inspection of the alloy G material in the mixing tube support system. This inspection of the existing material revealed minor attack. It should be noted that based on inspections several alloy experts indicated the anticipated life for alloy G was 20 years. Following completion of this review, it was decided to install a cladding of alloy G on all ductwork from the absorber outlet to the stack. During the first week in August, an order was placed for the alloy G which was to be used in the outlet ductwork. The coating failures that promulgated the change to alloy G could not be attributed to the closed-loop characteristic because up to this time problems in the plant's overall water balance necessitated running the gas cleaning system primarily in the open-loop mode.

During this same period of time, several coating experts visited the plant site and inspected the coating which had been applied to the absorber module itself. Upon visual inspection of this coating, an orange-red tint appeared over the surface with a crazing or cracking taking place on all walls. The original coating supplier stated that the failure was due to some sort of chemical attack and that he would not be willing to give any warranty or guarantee to his materials unless he could be given a complete analysis of what was in the slurry itself. The visual inspection also found that the glass fibers and fillers of the coating appeared to be dissolved while the binders were in good condition.

A continuation of the materials review examined the construction materials within the absorber module itself. It was determined that the replacement materials of choice would be rubber lining in the upper portion of the module from the first rod deck through the outlet dampers and alloy G (with a higher grade alloy as weld material) in the inlet nozzle and the lower portion of the absorber module where the possibility of high temperatures might exist. Removal of the old coatings, cleanup and installation of the rubber lining and the alloy G material started in January 1980. Two months later, modifications to the Unit 1 gas cleaning system were completed. The unit was placed back on line and the loop was closed for the first time on a continuous basis.

In conjunction with the March 1980 start-up of the Unit 1 gas cleaning system, a chemical testing program to verify system equilibrium was conducted by the absorber supplier. The test program continued for 30 days under the direction of the supplier at which time the South Mississippi Electric Power Association assumed responsibility for running the program. After 60 days of operation, system equilibrium had been verified. Table 2 presents the characteristics of this system as it existed in the closed-loop operation. Based on the successful operation of the unit during this 60-day period, it was decided to continue the chemical testing on a two-days-per-week basis so that system chemistry and sulfate saturation levels could be monitored.

TABLE 2. CLOSED-LOOP SYSTEM CHARACTERISTICS

| Ion Species | Range (ppm) |
|---|---|
| Calcium | 850 - 950 |
| Magnesium | 5,500 - 7,500 |
| Sulfite | 150 - 300 |
| Sulfate | 10,000 - 15,000 |
| Carbonate | 40 - 100 |
| Chloride | 12,000 - 15,000 |

One of the by-products of this chemical testing was a data base for determining system upsets and the characteristics of the Morrow Plant corrosion problems. For instance, it is now known that the choride level exceeded the range given in Table II and values in the 18,000 to 20,000 parts per million range occurred on an infrequent basis. It is also very easy to determine how tightly the overall water balance was maintained by studying the various levels of the ionic species.

While Unit 1 was off line for repairs, Unit 2 continued operation. After Unit 1 resumed operation, Unit 2 underwent similar modifications. In June 1980, Unit 2 was started up after completing the replacement of the corrosion-protection materials. The Unit 2 system was monitored on a twice-a-week basis just as Unit 1 was. From June through October of 1980, the availability of both units had been 100 percent and the corrosion-protection materials appeared to have been holding up. Actual inspections had not taken place because both units were on line continually.

In October, Unit 1 was removed from service for fall outage. At that time severe pitting existed on the floor of the absorber inlet nozzle, the access door ledges, and also in the mixing zone. All of these areas had been clad with alloy G. However, the horizontal run of breeching from the mixing zone to the stack appeared to be in good shape as did the alloy G which existed in the lower part of the absorber module.

## HASTELLOY ALLOY C-276

Because FGD system corrosion experience with alloy G was limited, it was very difficult to determine whether or not there was pitting. From the authors' vantage of hindsight, pitting in the horizontal run of the duct probably did exist, but could not be identified as such at that time. The pitting on the alloy G in the absorber inlet nozzle on the access door ledges and also up in the mixing zone was severe enough that additional cladding became necessary.

Due to the failure of the alloy G after approximately seven or eight months of operation, it was decided that a 1.59 mm (1/16-inch) cladding of HASTELLOY alloy C-276 be installed on the floor of the absorber nozzle, the access door ledges, and approximately 400 square feet in the mixing zone, and to give Unit 1 additional operating time to find out if the corrosion was a localized or general attack. The decision to use alloy C-276 was based on published literature, consultation with alloy suppliers who visited the site, and the excellent appearances of the alloy C-276 weld material used to clad the alloy G.

In a continuing effort to learn more about other materials that can resist corrosion in the FGD system environment, 500 square-foot test patches of a fluoroelastomer and an epoxy coating were applied to other areas of the vertical riser.

In December 1980, Unit 2 was brought off line. An inspection of the alloy G revealed that it was actually in worse condition than that in the mixing zone and the outlet ductwork of Unit 1. The 3.18 mm (1/8-inch) thick alloy G was completly perforated in the lower portion of the mixing zone after six months of operation. Due to this, the absorber inlet and most of the vertical riser of the mixing zone were reclad with alloy C-276. After these modifications, the unit ran for approximately three weeks, at which time it was brought down again. Inspection of the alloy C-276 on the absorber inlet nozzle showed minor or insignificant signs of pitting. It was decided at that time to bring the unit back on line and run for a substantial period of time before making any conclusions on either the coatings or the alloy material.

In April 1981, an inspection was made of the rubber lining in the absorber, alloy C-276, alloy G, and the fluoroelastomer and epoxy coatings which were applied to the vertical ductwork of Unit 1. The rubber lining was found to be in excellent condition. This inspection revealed definite corrosion, possibly crevice corrosion or very shallow pitting, in the alloy C-276 beneath sludge on the absorber inlet nozzle floor. In the mixing zone area of the outlet ductwork, alloy C-276 appeared to be in reasonably good condition but no conclusions as to its acceptability in this area have been reached. The epoxy coating appeared to be holding up. The fluoroelastomer coating had several bubbles of approximately one to two inches in diameter, but upon removal of the bubble it was clearly visible that the alloy G underneath had a severe pit under the center of the bubble, and that this pit probably perforated the alloy G. It was thought, at that time, that the fluoroelastomer was withstanding the conditions, but that the disbonding and thus the bubbling were due to gas expansion which existed between the alloy G and the carbon steel. Alloy G in the long horizontal run of duct leading to the stack revealed significant pitting, especially in the area closest to the stack. The lower portion of the absorber module which was clad with alloy G appeared in good condition.

## COATINGS - REEVALUATION

Due to the severe corrosion of the alloy G throughout all of the ductwork, it was decided to embark upon a test program to look at various coatings which could be applied to this ductwork. In May 1981, five different coatings were applied to various sections of the ductwork of Unit 1, making a total of seven coatings that could be studied after approximately six months of operation.

During the surface preparation for these coatings it was noted that the alloy G was in much worse shape than originally anticipated. Sandblasting to achieve the correct profile revealed that the pitting which existed throughout all the ductwork was much deeper and more severe than had been previously thought. Consequently, special precautions as to the surface preparation were used for the coatings. It was decided to use high pressure potable water to blast ductwork walls followed by a sand blast, a high-pressure neutralizer blast, another potable water blast, and then hot air to dry the surface. Subsequent to surface preparations and coating application, the unit was brought back on line.

After approximately five months of operation, the unit was removed from service to allow for inspection of the seven different coatings. The one epoxy-based coating held up very well with only a few small blisters visible. It should be noted that disbonding did occur in a few places but the base metal was still being protected and the coating material did not experience any acid attack. This blistering was blamed on faulty application. Three of the four fluoroelastomers appeared to withstand the chemical conditions, but due to the alloy G surface conditions, adhesion of this material appeared to be a problem. Later analyses of the disbonded fluoroelastomer indicated proper surface profile was not achieved on the alloy G. The glass block material exhibited signs of cracking but did appear to withstand the chemical conditions in the ductwork. Two coatings could not withstand the ductwork conditions and failed due to adhesion, chemical attack, temperature, or some combination of these.

## CURRENT PLANS

Based on the coating tests, it was recommended that epoxy-based coating be installed in those areas of Units 1 and 2 which showed the most serious signs of corrosion. The alloy C-276 will remain in place and will not be coated, thus allowing for a continual testing of that material. It was also recommended that several test patches of the different fluoroelastomers be installed to allow for further testing. In addition, an EPRI test program is being conducted on these units to allow for more testing of coatings and alloys. The coatings will be installed over a base carbon steel material so the results of this testing should be more applicable to new or retrofit-type installations. This EPRI test program will begin in April 1982 with the alloy testing in Unit 2. The coating will be installed on Unit 1 and it is anticipated that start-up of that unit will occur in June.

## SUMMARY AND CONCLUSIONS

What has been determined is that there is still a lot to be learned about closed-loop limestone FGD systems. In analyzing these problems it is important that a test program be set up to analyze the overall system chemistry and to try to determine those constituents in the flue gas which can cause corrosion with the high alloys. Based on the Morrow facility experience, the major problem areas with respect to alloy materials appear to be wet-dry interfaces either at the inlet to the module or possibly at bypassed and scrubbed gas mixing zones.

In both these areas, high corrosion rates of some of the most highly alloyed materials severely limit the availability of the FGD systems. Within the gas cleaning system itself, rubber lining appears to be a very suitable material while alloys are also acceptable as long as they are kept clean.

* * * * *

# FIBERGLASS REINFORCED PLASTICS AND THEIR SUCCESSFUL USE IN FLUE GAS DESULFURIZATION EQUIPMENT

by: Winston J. Renoud and Richard J. Lewandowski
Fiberglass Structural Engineering, Inc.
Bellingham, WA 98225

## ABSTRACT

Fiberglass Reinforced Plastics (FRP) have proven extremely successful over the last thirty years as a material of construction for large, self-supporting structures that contain acidic liquids and gases. Recently, the first coal-fired power generation plant FRP chimney liner, located at Maysville, Kentucky, was found to have an advanced corrosion problem and be in need of an immediate and extensive repair program. This paper discusses why the problem developed, what was done by the power company to correct the damage, and what was done to alter the corrosion and monitor future FRP chimney liner acceptability for service as a corrosion resistant structure.

FRP applications to flue gas desulfurization in general will be considered. Also, methods will be examined by which these applications can be evaluated and equipment put into service and maintained. Issues such as FRP's ability to resist fire, corrosion, and support loads for long periods of time will be considered. In addition, the power plant owner's level of involvement in design, specification, and construction inspection to adequately assure equipment success will be considered.

## INTRODUCTION

With the advent of Flue Gas Desulfurization (FGD) and the resulting cooler, wetter conditions in ducting and chimney liners, a whole new generation of corrosion and materials problems have appeared for the designers and owners of electric power generator plants. There are several alternative materials for this service, and none is clearly the best material. Fiber Reinforced Plastics are a highly corrosion-resistant and cost effective possibility for the construction of this equipment. Large size Fiber Reinforced Plastic (FRP) equipment has been operating in similar corrosive environments in the chemical, pulp and paper, and mining industries for many years. In this paper, the corrosion conditions in flue gas exhaust systems are briefly examined, as well as the strengths and weaknesses of alternative corrosion-resistant materials. Next, the recent repairs and conditions leading to these repairs at East Kentucky Power Cooperative's Spurlock Power Station FRP chimney liner are discussed. Finally, an engineering approach by which plant owners can most successfully purchase and use FRP equipment for flue gas desulfurization is suggested.

FRP scrubbers, duct, and chimney liners have been used for many years in severe corrosion conditions. The size, complexity, and service conditions of this equipment is similar to that which is presently used by the power industry for scrubbers, duct, and chimney liners. Figure 1 shows a 25 foot diameter FRP absorber and associated duct. The FRP absorber walls support metal internals and are designed for Seismic Zone 3 and 350 degrees Fahrenheit operation. Figure 2 shows a segment of a 32 foot diameter scrubber being installed. This vessel basically consists of a horizontal tank filled with internals. The gases enter the vessel through a large dual-throated venting scrubber. Figure 3 is a 24 foot diameter chimney liner 1,215 feet tall. It is the tallest FRP chimney liner in the world. This information is presented to demonstrate the technology that exists for corrosion-

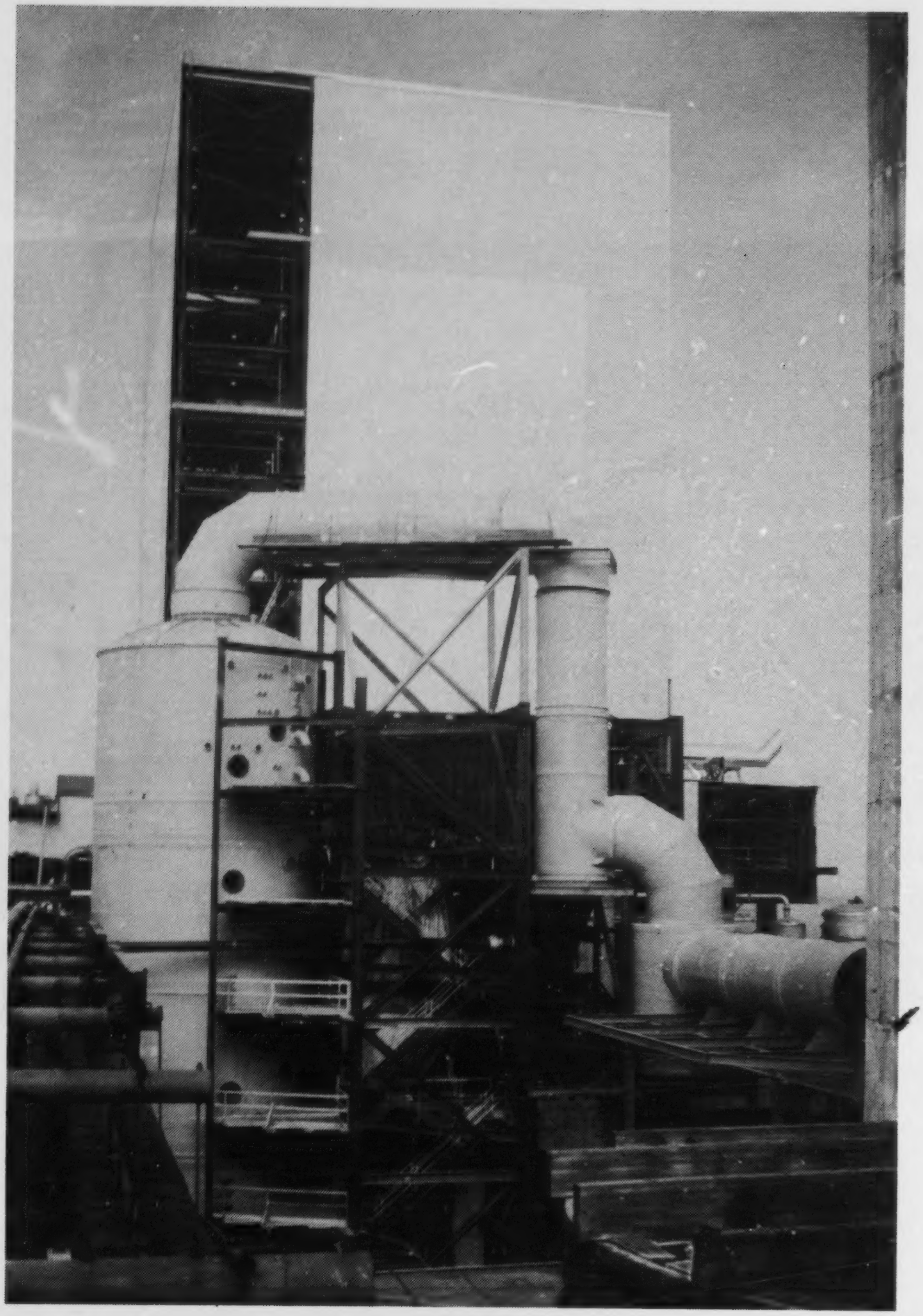


Figure 1. 25'0 Absorber; 63' tall, 350° design temperature

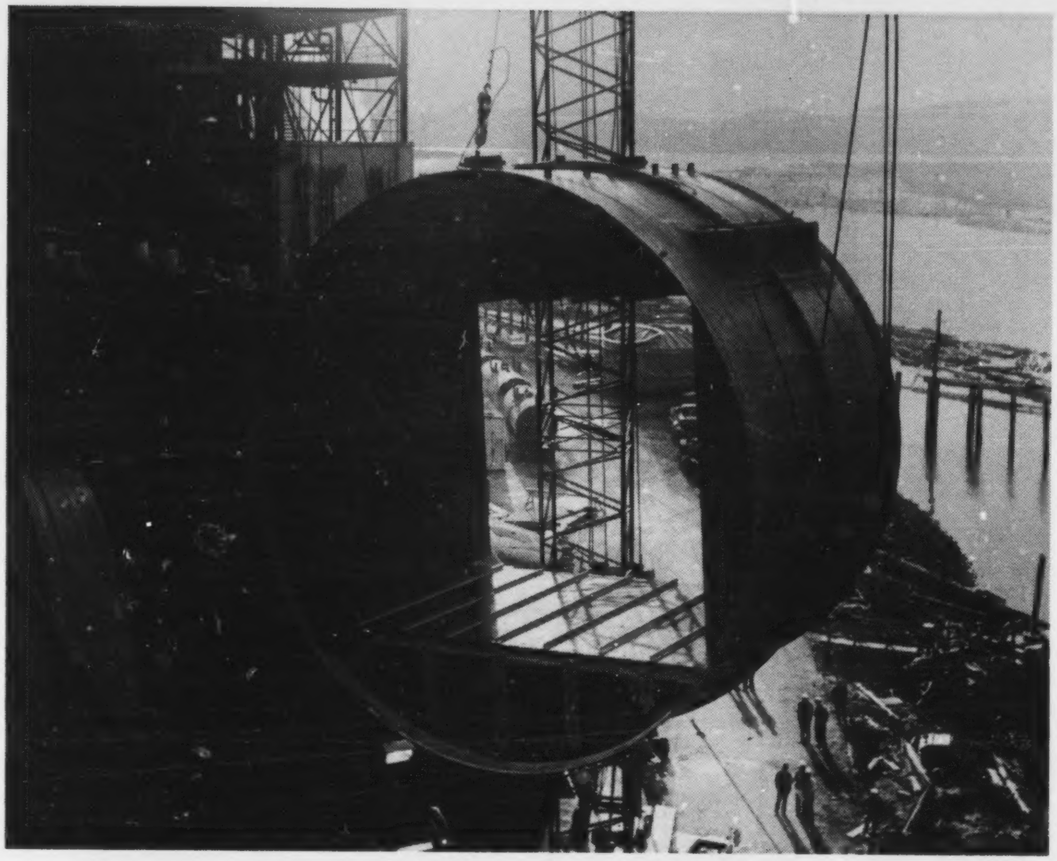


Figure 2. Segment of 32'Ø Scrubber during installation

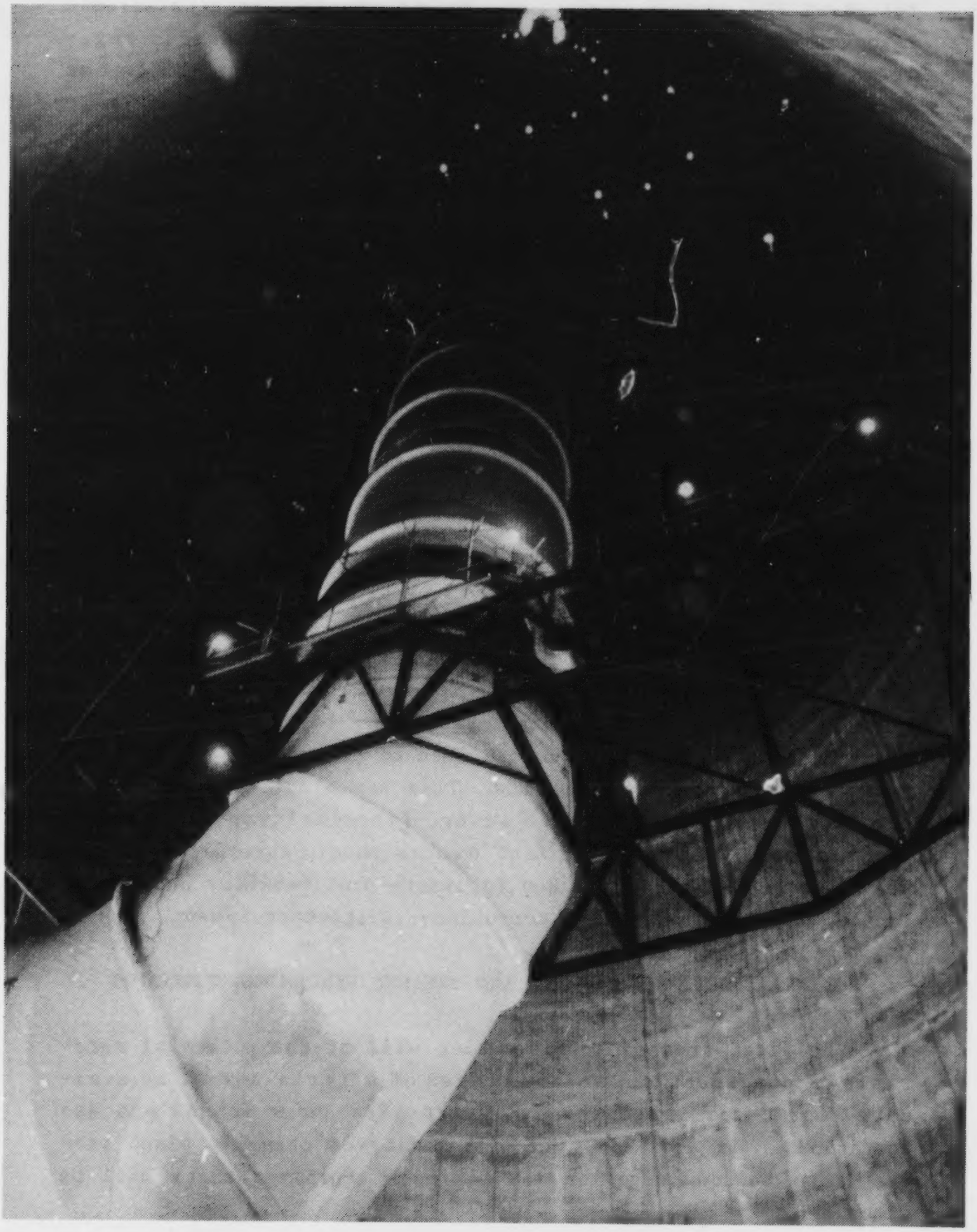


Figure 3. 1,215' tail FRP Chimney Liner, 24'Ø

resistant FRP process equipment. This technology is an available resource for the electric power industry. When materials engineers for a flue gas exhaust system determine that FRP is the preferred corrosion-resistant material of construction, then there is a proven technology for design and construction of the equipment.

The plant owner or his representative has typically used process companies or equipment suppliers as consulting engineers in the design of process equipment. This has been necessary because the owner has not had the technology or manpower available to control the design and construction by himself. As a result, the equipment supplier makes the decisions about the key aspects of the equipment. These decisions are regulated and controlled somewhat by industrial standard. For simple materials systems, this is a reasonable course of action.

In this paper, we will suggest that with Fiber Reinforced Plastic process equipment, it will be profitable for owners to maintain tight design and construction control rather than depend upon the equipment supplier. This is desirable because of the difficulty and complexity of design and construction of the equipment and the lack of industrial standards. Improper design decisions or construction methods can lead to greatly increased maintenance and reduced service life. This has almost no effect upon the contractor, yet can have severe financial impact upon the plant owner. Therefore, plant owners should carefully consider the engineering approach taken to assure profitability and satisfaction in their use of FRP corrosion-resistant equipment.

## POTENTIAL MATERIALS OF FGD AND EXHAUST SYSTEM CONSTRUCTION

The first area of consideration will be the potential materials of construction. Various types of materials will be evaluated for their strengths and weaknesses under actual process conditions. In addition, the possibility of changing plant processes to reduce corrosion and minimize equipment costs will be discussed.

A review of various plants' scrubber, duct and chimney liner conditions shows that no two systems are exactly alike. As a result, each system, the components of each system, and the conditions under which each system operates must be analyzed on a case-by-case basis.

Abrasion, acid, and chlorides are destructive to all materials used in scrubber construction (see reference 1). For duct and chimney liners, operation is often below the sulfuric acid liquid-gas equilibrium line (Figure 4). Normal operating temperatures range between 200 to 450 degrees Fahrenheit, making any acid concentration between liquid gas transformation and 103.5% $H_2SO_4$ possible. The partial pressure of water vapor and $SO_3$ will determine the steady state concentration of acid occurring in a system. As the temperature of the gases, condensed $H_2SO_4$ and water increases, the acid concentration and corrosion of the container walls increases rapidly. A greater concentration of $SO_3$ with respect to water vapor will increase the concentration of sulfuric acid in the system, speeding corrosion of the equipment.

Relief from corrosion can be achieved by lowering the temperature or by reducing the $SO_3$-to-water vapor ratio of a system. Each of these methods will lower the concentration of corrosive sulfuric acid. Another possible method of corrosion relief is to increase the temperature of the gases to the point that sulfuric acid would vaporize rather than remain in its liquid state. The sulfuric acid would be eliminated and corrosion would cease.

Several construction materials are available for FGD systems, ducts, and chimney liners. These include highly corrosion-resistant metals, thermosetting plastic coated steel, brick, and fiber reinforced thermosetting plastics. There is no perfect material. Each material has its strengths and weaknesses that affect the life cycle cost of the equipment. Selection of construction material and equipment engineering will determine original equipment cost, cost of repairs, and lost production time over the life of the equipment. Lost production can be a major expense and, as a result, reliable performance of the duct and chimney liner is critical. In contrast, unexpected failure and repair of scrubbers is less serious, but only if the scrubber can be completely bypassed. These considerations of life cycle cost and production interruption become the basis of materials selec-

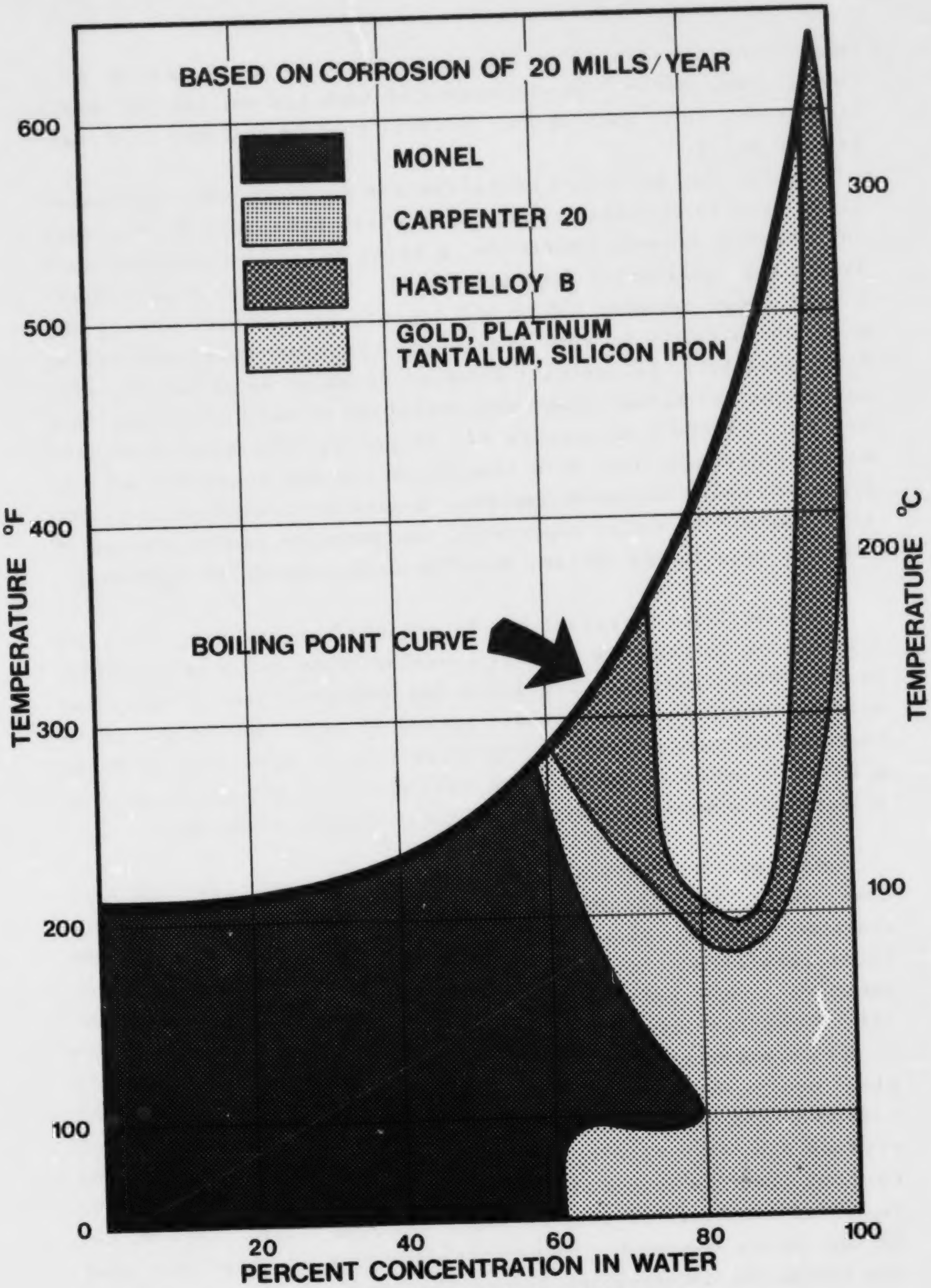


Figure 4. Metal Alloys for Sulfuric Acid Service

tion and later equipment design.

## METALS

The primary strength of metals for FGD and exhaust system construction is that most noble metals have very high resistance to corrosion by concentrated sulfuric acid at elevated temperatures. It is apparent from Figure 4 that metals such as gold, platinum, tantalum, silicon iron, Hastelloy B, Carpenter 20, and Monel exhibit low rates of corrosion. Among these metals, Hastelloy B and Carpenter 20 are practical for use in ducting and chimney liners, and are most likely to survive in high concentration sulfuric acid conditons. (For candidate materials for the construcction of scrubbers, see reference 1.) Equipment made from metals have a monolithic single material wall with no voids or defects except in the area of welds, which is a great advantage in minimizing corrosion. Furthermore, the structural qualities of metals are excellent with proper design. The technology for design and construction of these metal structures is well developed, standardized, and widely known in the engineering community.

The principal drawback of highly corrosion-resistant metal equipment is cost. Metal equipment can be two to four times more expensive than the alternatives. Secondly, materials availability could be a construction problem. One large chimney with two liners, for example, would require a large percentage of the total annual U.S. production of Hastelloy B. Quality of the finished equipment, furthermore, requires very precise fabrication, particularly in making necessary welds. Metals are also more sensitive to process changes and the introduction of new materials, such as chlorides, than the other materials considered. Finally, when the interior of the metal equipment wall is corroded away, there is no simple method of repair. In most cases, equipment replacement is the only solution.

## STEEL WITH A REINFORCED THERMOSETTING PLASTIC COATING

A mild steel structural wall with a reinforced thermosetting plastic coating can be installed at relatively low cost. Another strength is that the basic reinforced plastic material is highly corrosion-resistant. In sulfuric acid service, plastic corrosion resistance can be seen on Figure 5. Also, changes in process such as the addition of chlorides have little effect on the corrosion rate of this plastic coating. As long as the structure is properly designed and corrosion does not penetrate the coating and start on the metal wall, the system should be structurally very stable. Availability of these materials is not a problem.

There are three important weaknesses of the plastic-coated metal system. This is an example of non-monolithic wall construction in which the material characteristics of the metal structural wall and plastic corrosion-resistant inner layer are significantly different. In FGD, duct or chimney liners which are improperly constructed or where temperatures cycle or remain high, plastic coatings can delaminate from the metal substrate. Secondly, small local defects in the lining are very likely to occur, and the need for repairs should be expected. Once coatings start to leak and allow liquids to reach the steel structural wall, rapid damage is possible. For chimney liners, access for regular inspection and repair is difficult and costly. The final problem is that the success of the lining is very dependent upon construction quality. The skill of the applicator is an important issue because any major mistake systematically performed will cause the lining to be of little or no value in protecting the substrate steel.

## BRICK

Brick is certainly the oldest material of construction in the post-boiler flue gas system. Chimneys have been made and lined with brick for many years, and brick is familiar to the power and construction industries. Power plant owners know that periodic inspection and repair are important, and there are numerous resources available to conveniently care for the maintenance needs. The materials for construction of brick vessels, duct, and chimney liners are plentiful and very corrosion-resistant.

The primary problem with brick chimney liners is the possibility of reduced structural integrity with the effects of service. There is special concern in areas of possible seismic

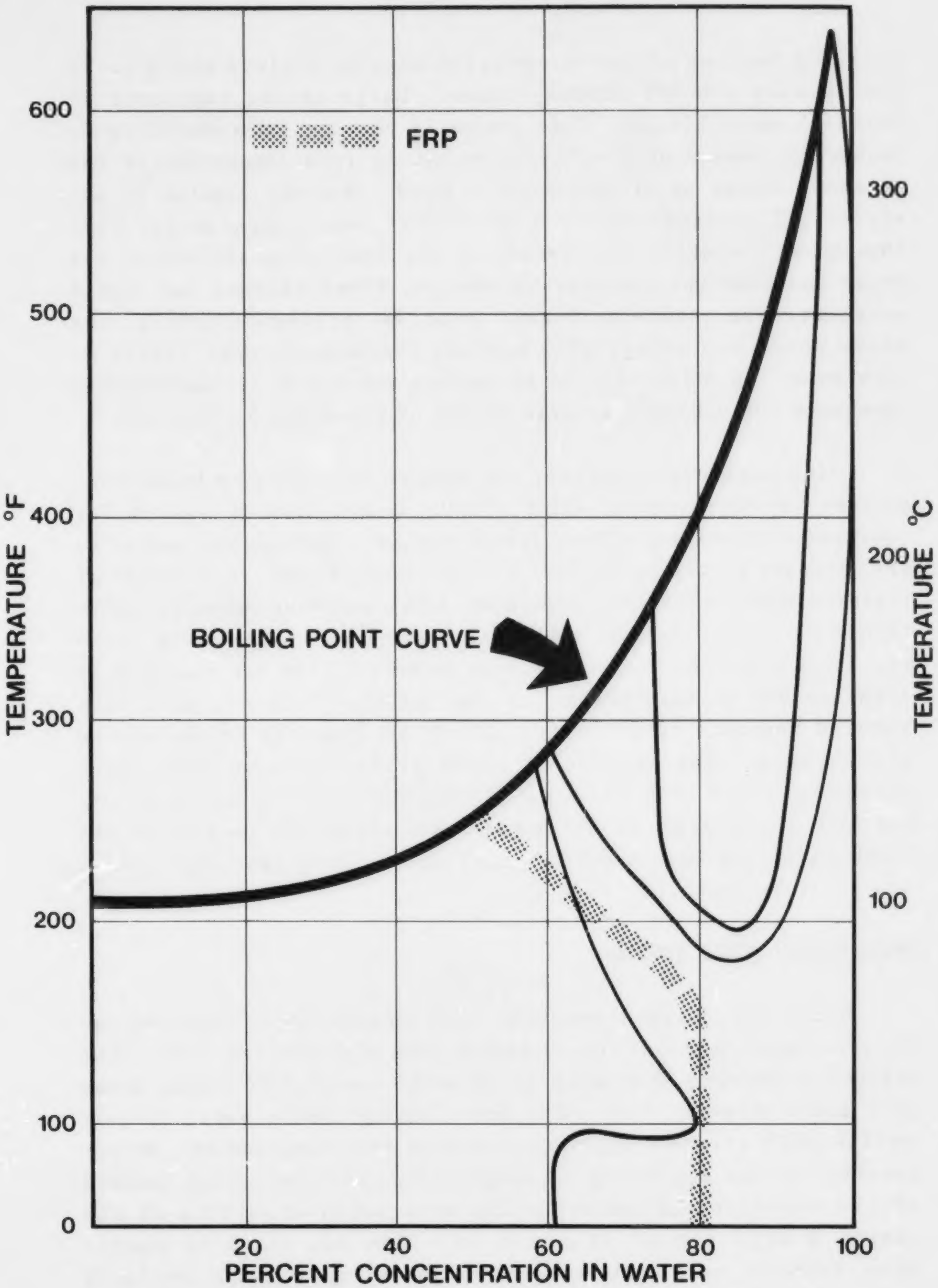


Figure 5. FRP for Sulfuric Acid Service

activity because of the potential damage or failure which could result with a brick chimney liner. Large cracks can occur in brick chimney liners. This probably results from swelling or geometric changes of the bricks resulting from absorption of the process liquids or temperature changes. Process liquids do not affect all surfaces of the brick evenly, and temperatures vary throughout the brick as a result of the insulating ability of the brick and flue gas temperature changes. These thermal and liquid concentration gradients result in stress gradients through the brick which may change with process conditions. The inside or outside of the brick will be in tension and result in crack formation when the ultimate tensile stress of the brick is exceeded.

With corrosive service, the mortar or mortar to brick connection may deteriorate, which results in the loss of support for individual bricks and allows liquid movement through the mortar to the exterior of the brick lining. In recent years, as a result of positive draft chimneys, equipment designers have opted to maintain a positive pressure in the air space between the brick chimney liner and the concrete chimney column. This has resulted in less leakage through the mortar or defects. This may also have reduced the rate of corrosive attack between the brick and the mortar area. The outside of these pressurized annulus brick liners does not leak freely as in the past, but is still moist. The rate of corrosion of the metal bands around the outside of the brick liner has been reduced, but three to five year replacement may still be expected.

## BRICK-LINED STEEL VESSELS

Brick lined steel vessels, with proper care, have demonstrated excellent corrosion resistance and service life. The effects of service on a brick lined metal vessel differ from those of a brick chimney liner. The brick lining inside metal vessels swells with service exposure and goes into compression. Structurally, bricks are strong in compression, and the curved surface of the vessel contributes to the structural stability of the lining. A major concern is mortar deterioration, which is repairable. Probably more serious is possible leakage through the brick and membrane layers to the steel vessel wall. Corrosion of the

metal wall can result, and replacement of the damaged metal wall, membrane, and brick lining may be necessary. In some cases, plastic repair materials can be pumped through the metal wall into the damaged area between the metal wall and brick. In the case of vessels or chimney liners, as with all other high performance, corrosion-resistant materials systems, design details and quality of construction are critical to success.

## FRP

Fiber Reinforced Plastic (FRP) is similar to metals such as Monel in its corrosion resistance in sulfuric acid (see Figure 5). Plastics have in many cases (such as with chlorides) much greater corrosion resistance than metals, especially when unexpected changes in the composition of the corrosive occur. The entire FRP wall is a monolithic material similar to metals. Although the wall consists of one continuous similar materials system, there is greater resin content for corrosion resistance near the corrosive side and more glass in the structural portion of the wall for strength and stiffness. Resin type, glass content, and glass orientation can be modified at various levels in the equipment wall to produce whatever wall capabilities are necessary. FRP is also a good structural material for supporting long-term loads at temperatures in excess of 300 degrees Fahrenheit, and the materials of construction are readily available. Sudden losses of structural integrity or corrosion resistance are unlikely in properly designed and constructed FRP equipment. If a problem develops with the corrosion-resistant inner layer, repair methods have been established. Another strength of FRP is that, although its performance characteristics are similar to metal, the cost is significantly less.

The weakness of FRP is that it is a complex material from both a design and construction standpoint. This is a result of the extreme design flexibility available. Along with the freedom of adjustment in design comes the responsiblity for skill and control. Although the design and engineering of FRP structures is well developed as a speciality, there are few industry standards and few qualified engineers. The many quality issues involved in FRP process equipment must be carefully addressed in design, specified in detail, and monitored carefully by knowledgeable inspection in shop and field construction. The last basic problem with FRP is that it is not as corrosion-resistant as the most noble metals in the most severe sulfuric acid conditions (Figure 6). Some chimney liners operate in the range of more than 80% sulfuric acid at greater than 200 degrees Fahrenheit. The corrosion-resistant FRP inner layer will corrode in an ablative fashion at about 10 to 30 mils per year under these conditions. In order to reduce the corrosion rate, the acid concentration and/or temperature may be reduced or more exotic materials used.

## MATERIALS SUMMARY

In conclusion, highly noble metals are very attractive for the construction of corrosion-resistant scrubbers, duct and chimney liners in every way but cost. FRP has performance capabilities which, for these applications, may equal or exceed metals except in very high concentration sulfuric acid. The cost of FRP is much less than these exotic metals and the materials are more available, but FRP is more complex to design and build. Power plant operators know what to expect from brick, and with proper maintenance, brick can be a very reliable lining for equipment located in non-seismic areas. Coatings are inexpensive and can provide some element of protection to the interior of metal vessels. In any case, the perfect materials system for FGD, duct, and chimney liners does not yet exist. Proper materials selection, equipment specification, and construction are critical to the success of these high performance materials for service in very hostile environments.

It may be very attractive or necessary to use FRP for a particular application due to seismic, reliability, or cost considerations. It may be necessary to modify a highly corrosive environment in the liner to use FRP successfully. Process changes can be made to assure long-term corrosion resistance of the FRP liner. In nonscrubbed operations, the concentration of $SO_2$-$SO_3$ can be reduced by the introduction of a reactive chemical such as ammonia. Another alternative is the reduction of sulfur in the coal or the increase of moisture in the chimney, which will reduce the concentration of the condensed sulfuric acid. Finally, the

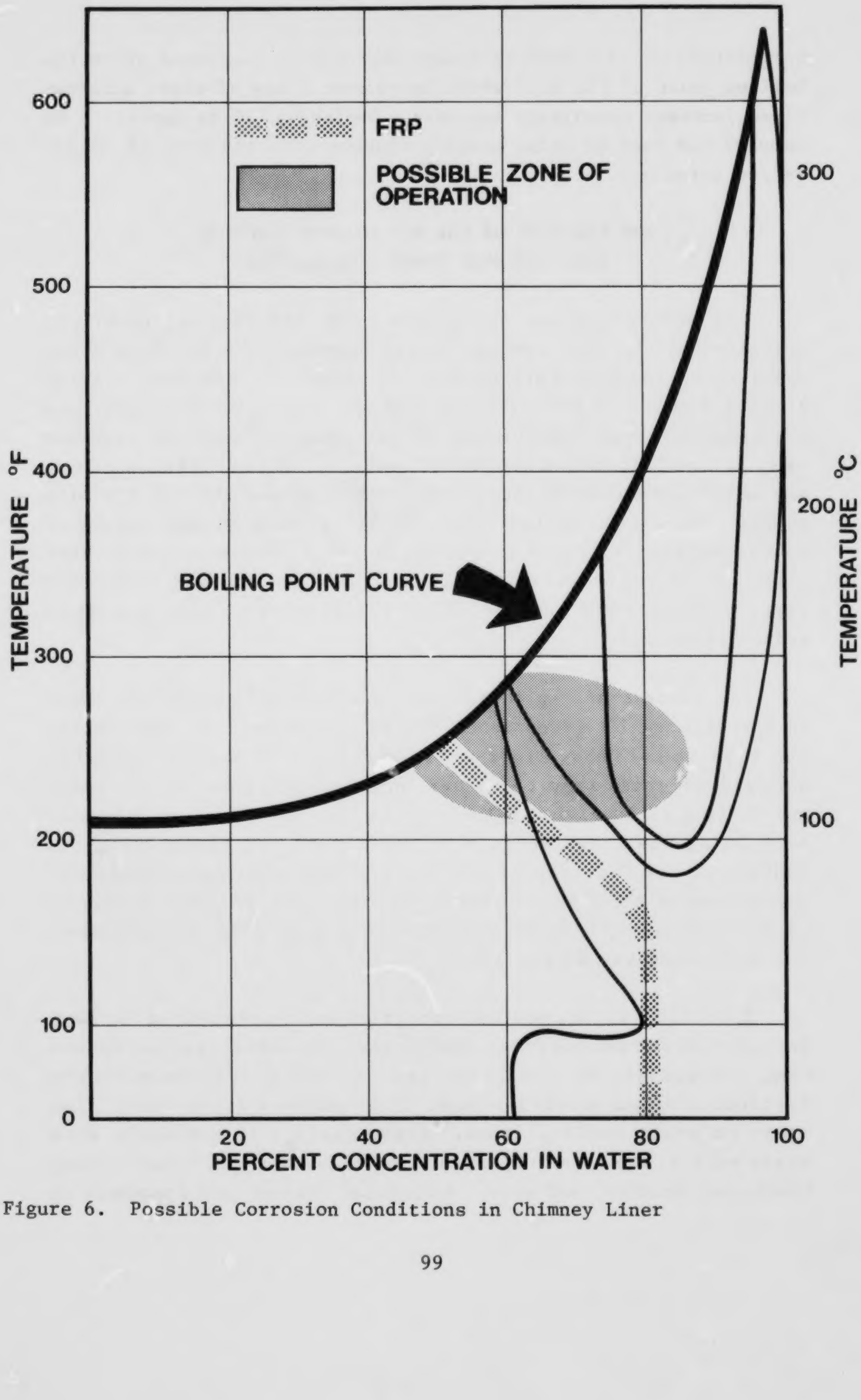


Figure 6. Possible Corrosion Conditions in Chimney Liner

temperature of the chimney liner wall can be increased above the boiling point of the acid which is present. Any of these alternatives increase complexity and cost. Obviously, it is important to compare the cost of these process changes with the cost of alternative materials.

## THE RELINING OF THE FRP CHIMNEY LINER AT EAST KENTUCKY POWER COOPERATIVE

The electric power industry's first FRP chimney liner was installed in the East Kentucky Power Cooperative's Spurlock Power Station, an 800 foot tall chimney at Maysville, Kentucky. After about 3.5 years of actual operation, it was determined that the corrosion-resistant inner layer of the chimney liner had corroded away at the bottom and should be replaced. The thickness of the new corrosion-resistant layer was to be between 140 and 150 mils at the bottom. The actual layer installed exceeded this thickness up the entire length of the chimney liner. This would provide from six to eight years of service life at the old corrosion rates. Plans were made to alter the process to significantly reduce this rate.

The process of replacing the inner corrosion-resistant layer of the chimney liner consisted of the following: 1) washing the ash from the chimney liner wall interiors; 2) sandblasting the damaged material from the liner interiors; 3) touch up grinding and filling of local irregularities in the chimney liner interior; 4) priming the inner surface of the liner; and 5) applying the coating to the interior of the liner. This coating consisted of approximately 3-1/2 oz. of random chopped glass mat, two 10 mil c-glass surface veil, and a surface resin coat with wax additive. The resin used was Hetron 197-P.

A quality assurance (QA) program was implemented by East Kentucky Power Cooperative (EKPC) and its consultant to assure that the quality of the relining, in fact conformed with the fabricator's own specification. This program first identified every relevant quality issue. These quality issues dealt with areas such as surface preparation, materials type, final lining thickness, quality, and cure. Inspection methods and frequency of measurement were established to monitor the lining activity. A substantiated written record of the quality of the work in progress or completed was developed by the QA program. This consisted of independent observations by QA or verification of the contractor's observations and written record of quality. This record for each quality factor was then compared with the acceptance levels stated in the contractor's specification or provided by the materials supplier. A decision was made to accept or reject the work based on this acceptance level.

Finally, provision for long-term observation of the key quality factors was made by EKPC. The company established methods of observing corrosion rate to the inner surface, chimney liner wall temperature at various levels, ash load, and performance of the liner as a self-supporting structure. These items can be monitored over time to develop predictive capabilities. This will provide the basis for planning future equipment maintenance or repair. Also, when process changes are made, the change in corrosion rates can be monitored to determine the effect of these process changes. This type of information is critical in making appropriate engineering decisions about FRP equipment.

## AN ENGINEERING APPROACH FOR THE BEST RESULTS IN THE USE OF FRP CORROSION-RESISTANT EQUIPMENT

If failure of FGD, duct, or chimney liners occurs prematurely, the plant owner is by far the greatest loser. This holds true regardless of the manufacturer's warranty. Clearly, the plant owner needs to know that the equipment he purchases will provide long service with minimal maintenance. His responsibility is to assure that adequate quality is designed and built into his FGD, duct, and chimney liner system. A plan for monitoring equipment quality as it is used is also necessary in performing timely maintenance and repairs.

As indicated earlier, a problem with FRP is the high number of engineering details and quality issues affecting design and construction. Our experience shows that the plant owner should maintain direct control over the design, construction and maintenance of FRP equipment. We suggest the plant owner consider the following steps in his use of FRP equipment: (1) Detailed design and specification of the system; (2) bidding based on detailed design and specification; (3) purchase order based on detailed design and results of bidding; (4) acceptance or rejection of fabricated equipment based on the detailed design and specified acceptance criteria; and (5) periodic maintenance inspections.

It is of the utmost importance that the power plant owners develop the detailed drawings of the process equipment system and the FRP components prior to bidding by the contractor. It is important for the equipment details to reflect the quality considerations that only the purchaser can determine. No one else can identify the purchaser's detailed FRP design needs in as unbiased a manner as the purchaser himself or his independent engineering representative.

Adequate time must be scheduled for project engineering. In practice, overall project schedule is normally reduced by the time savings produced in detailed design at the start of a project. Once the actual process is defined, the equipment designers can then work with process engineering to create the best system possible, incorporating process, operations, and maintenance considerations within the budget and real estate allocated. In most cases, the overall system is greatly affected by the details of its components. As a result, the optimum system is usually developed through an interactive process. A total system using both FRP and metals can achieve an optimum balance of quality and cost. Once the overall system is established, the details of the FRP FGD equipment, ducting, chimney liner, and support steel can be completed. Owner control over this detailing is often the difference between success and failure. Detailing is the most difficult work, but quality depends completely upon the amount of effort expended on these details. Decisions regarding construction details must be made; if the owner or his representative does not make them, they will certainly be made by someone much less qualified to make those decisions. Not to define important details which affect quality is tantamount to writing a blank check to the contractor-fabricator.

Basic considerations in the development of quality FRP equipment include:

1. Description of equipment process and service conditions as the basis of equipment development.

2. Materials selection and design of the corrosion-resistant interior and exterior liners based on service conditions.

3. Development of FRP, metal, and concrete support systems which will provide reliable support for themselves and the operational loads expected over the equipment life span.

4. Finally, all these considerations must be integrated into a total design which provides the best possible balance between life cycle value and risk of equipment failure. The design must be recorded in the form of detaildrawings andspecifications which exactly describe what is to be constructed so that any qualified fabricator can clearly understand understand exactly what to bid and fabricate.

The equipment design parameters must be carefully and completely defined. Every step in equipment development is dependent upon the accuracy of each previous step. If incomplete and unrepresentative design criteria become the basis of later equipment development, there will be increased risk of equipment failure and decreased life cycle equipment value. These errors will continue throughout the development process and be reflected in the final equipment. Great care should be used by the FRP engineer and process designer so that all conditions which could affect equipment corrosion or structural integrity can be accurately defined.

The design conditions should reflect maximum operating conditions and realistic upset conditions. These upsets may result from unexpected loss of water, power or sewage removal. Transient conditions during startup, shutdown, or process excursions may produce extreme conditions well beyond those of normal operations. High loads can also result from winds or seismic conditions. It is interesting how often the unlikely occurs. The loss of the Hood Canal floating bridge in Northwest Washington during the Spring of 1979 was probably the result of several different natural extreme conditions which allegedly "couldn't occur simultaneously." These conditions did occur and the bridge sank. Also, if process conditions have a reasonable chance of being altered in future process changes, this should be taken into account in establishing the equipment design criteria.

There may be several different combinations of design conditions which need to be stated. Design conditions are used first as the basis for materials selection and design of the interior and exterior corrosion-resistant liners. Secondly, the design conditions will be used as the basis for structural design. In both cases, different types of information are necessary. Also, for the various upset or extreme conditions, there are different possible combinations of maximum pressure, temperature, process chemistry, etc., which should be completely stated for each condition.

Once the various combinations of design conditions are finalized, the design of the interior and exterior corrosion-resistant liners can be done. The polyester/vinylester family of resins are sensitive to extremes of the following: (1) Temperature; (2) abrasion; (3) high strain levels; (4) organic solvents (especially aromatic types); (5) fluorides (when glass reinforcing is used); and (6) strong oxidants.

These conditions must be very carefully defined and considered during materials selection and liner design. Various combinations of resin systems and reinforcing can be used to provide the maximum in-service life for the proposed equipment. Abrasion resistant fillers can be used to reduce abrasion. Many times, unusual problems involving degradation of equipment wall surfaces can be reduced or eliminated by changes in process or equipment which will not significantly affect process profitability. Further, it is often valuable to consider potential equipment impact as one of the process development considerations. Tests of various candidate liners in simulated or real conditions is a conservative method of defining which laminate would be optimal for corrosion resistance in the proposed service.

Also, corrosion resistance of external metal or concrete support structures should be considered. This area is frequently overlooked. In many cases, process equipment is produced for a 10 to 20 year service life, whereas the metal or concrete support structures have only 5 to 10 years of useful service life with no simple method of replacement. Premature failure of external support structures can accelerate the degradation of the highly important FRP process equipment.

Structural design of the FRP equipment and metal and concrete support should be done simultaneously to provide the most integrated system possible. The primary considerations are: (1) The proposed shape of the equipment to be produced; (2) the loads to be supported; (3) the operational conditions which will affect the short-term or long-term load bearing capabilities of the equipment walls; and (4) the proposed life span of the new equipment.

The size and shape of an FRP structure directly affects the difficulty in developing a structural design to support the proposed loads. The approximations and theoretical accuracy acceptable for small structures becomes completely unacceptable with very large engineered structures, such as are found in FGD. Also, certain traditional approaches used to compensate for increased size produce poor results when used on very large structures. There must be accurate mathematical models used for structural analysis of large structures. In many cases, large equipment must be constructed in structure modules to facilitate support and production. By taking a large, unmanageable problem and breaking it down into small, manageable units, problems of scale can often be overcome. This has been done on large scrubbers and very tall chimney liners.

Large flat areas or straight structures with loads oriented perpendicular to the structure are also difficult. These loads can be efficiently handled by the use of curvilinear surfaces or deep section structural members.

Some of the loads to be supported may be due to the following: (1) handling; (2) maintenance (people, scaffolding, etc.); (3) unusual internal weights as a result of backups of process liquid (plugged packing or drains) or unexpected buildup of solids; (4) peak vacuum conditions (even slight for large structures); (5) peak pressures (which may result from an unexpected flow restriction and resulting peak fan or pump pressures); (6) wind or seismic conditions; (7) external loads such as snow, agitators, external liquid buildup, ladders, handrails, or grating; and (8) internals or vessel contents. The total structural system must have a reasonable chance of supporting the most severe of these loading conditions on the last day of the proposed service life.

Both the short-term and long-term load bearing ability of the structural portion of the FRP walls is affected by exposure to service conditions. In the short term, temperature affects modulus of elasticity and strength, and produces residual stresses between plies of varying glass content. Temperature increases reduce modulus of elasticity (MOE) at a steady rate up to the heat distortion temperature, beyond which the MOE of many resin systems decays rapidly. FRP strength in the short term is affected less severely by increased temperature than MOE.

Long-term tensile load bearing ability of FRP is dependent upon time and severity of exposure. Leakage of process liquids through the corrosion-resistant barrier, extreme corrosion (external or internal), and high temperature or operational stress levels may result in rapid long-term reductions in the tensile load bearing ability of FRP. This reduction in physical properties through exposure to service is traditionally compensated for in design by providing a nominal design factor on fracture for new laminates of ten times. When laminate strength is reduced through service to nearly the minimum necessary to support peak loads, leakage, laminate crazing, and possible catastrophic collapse of the structure will occur. Hopefully, wall deflections and/or leakage will warn the operator so that the equipment can be taken out of service prior to catastrophic collapse. This requires regular equipment inspections by qualified inspectors.

It is important to understand the reason for the initial design factor of ten on fracture.[1] Service effects reduce this design factor through the FRP equipment life. For strength limited laminates, design factor on fracture has become the basis of design. The larger the initial design factor, the longer the structural walls will support the equipment loads before failure.

The second basis for establishing the design stress is the maximum allowable laminate strain at a specified number of cycles. The corrosion-resistant liner will deteriorate when cyclically loaded, especially in the presence of corrosive media. With a peak strain of 0.1 to 0.2% for a typical brittle corrosion-resistant polyester mat laminate, fracture will occur in about $10^7$ to $10^8$ cycles.[2] As a result, for laminates, such as filament wound (ASTM D3299), the maximum allowable strain becomes the basis of design. The lower the peak strain, the more cycles to failure of the corrosion-resistant liner, which represents the end of the equipment life.

For compression, the design stress is normally based on the critical strain to elastic instability reduced by some safety factor. If the real physical system is accurately modeled by the designer for short-term periodic compressive loads, a relatively low safety factor may be used. However, if continuous long-term compressive loads are expected, then fairly high initial design factors are necessary. The reasons higher design factors are necessary for long-term compression is the compressive creep which occurs in FRP structures. This creep is affected by service conditions, such as presence of moisture, temperature, nature of laminate, stress level, and time.[3] The sum of the elastic deflection due to live load and long-term creep deflections will eventually approach the critical deflection necessary for elastic instability and collapse. The higher initial design factor allows a longer period of time for service life. As elastic instability approaches, the equipment walls become wavy. An experienced inspector will see this occurring and initiate replacement or modifications of the equipment before collapse occurs.

When first introduced to FRP structures , most engineers are surprised by the high design factors used. These design factors are so reduced by service effects and time that to produce a reasonable service life, they must be initially large. The objective is to design vessels which have appropriately balanced design factors, good corrosion resistance, and which are cost-effective.

Ideally, at the end of the proposed service life, the reduced strength and integrity of the process equipment will remain sufficient for the working loads imposed by normal operation. This is the most fundamental structural design goal. Resistance to degradation will be gained by quality materials (resin and glass) and care in laminate design to protect the higher glass reinforced structural walls from exposure to corrosion. Interestingly, the laminates most resistant to service exposure (high resin laminates, such as all mat) are structurally inefficient due to their low strength. Efficient high strength, high glass laminates are rapidly affected by exposure to some service conditions. Laminates must be developed by the equipment designer which allow the best balance between structural efficiency (initial high strength or modulus) and resistance to design factor loss from service effects.

Only brief discussion of the actual equipment structural design will be possible in this text. We will look at the methodology used to size cylindrical holding tank wall thickness for hydrostatic head. Every design consideration requires this type of thorough evaluation. Good design does not just happen, it depends upon a systematic, factual approach.

Modulus of elasticity (MOE) is an important parameter which must be accurately known to design filament wound FRP tank walls. Both tension and compression laminates are designed on strain unless strength requirements are exceeded. The modulus of elasticity of an FRP laminate in a particular direction is proportional to the ratio of glass and matrix (resin) in the proposed direction of loading. For example, with a 70% glass content by weight, there is about 50% by volume of both glass and resin. The MOE of the glass fiber alone is $10.5 \times 10^6$ lb./in.$^2$ and for resin is $0.5 \times 10^6$. For a 70% glass by weight laminate with all glass fibers parallel, the composite MOE in line with the glass is the mean of the MOE's of the constituents, or $5.5 \times 10^6$ lb./in.$^2$. This now becomes the basis of design for filament wound (a = 90 degrees) tanks and vessels. This could be used in conjunction with the 0.1% strain allowable in ASTM D3299 to provide a design hoop stress of 5500 lb./in.$^2$ for the filament windings only. The vessel wall would be sized for the necessary filament winding thickness and interior and exterior corrosion-resistant layers would be added, assuming they add no structural contribution. This example roughly demonstrates the line of logic necessary for the design of a vertical filament wound vessel wall based on circumferential tension and certain laminate assumptions. In addition, it is necessary to consider the effects of internal pressure, vacuum, seismic, agitators, localized stress risers or concentrations, such as penetrations, changes in curvature (top and bottom knuckles), and hold down lugs. Certain laminate assumptions must be made to establish load bearing capacity of the wall and the various potential failure modes analyzed to determine the critical details (such as thickness) of the design.

The considerations which should be kept in mind, however, are that FRP has a low modulus of elasticity, is anisotropic, and has relatively low strength which is affected by time of exposure to process conditions and changes in temperature. This makes the design of FRP equipment significantly different from that of metals or other traditional materials.

Finally, detailing of FRP vessels and support structures is of the highest importance. Most critical quality attributes are determined and specified in the detail drawings. It would be better not to firm price than to not firm construction details. Design detail and price must both be defined precisely and concurrently.

Once the final design is completed, we are adequately prepared to objectively enter the turbulent activity of fabricator and contractor bidding. The detailed design promotes competitive bidding among qualified bidders on the basis of complete and unequivocal information. This minimizes misunderstanding, cost, and time involved and maximizes the fairness, ease, and objectivity of bid evaluation and vendor selection.

When the purchase order is prepared, the detailed design provides the basis for a complete legal description of what is to be supplied and at what price. This minimizes the time and work to prepare the purchase order. This clear, complete, and fair contract provides a stable basis for the management of the remainder of the project.

In the equipment acquisition activity so far, it is assumed that the FRP equipment will have certain quality attributes which will allow the system to perform up to expectations. However, all the planning in the world is useless unless the equipment meets the minimum requirements of the design and specification with a minimum of rework. The qualified fabricator must have a production plan by which equipment can be produced which will have the qualities of the equipment described in the purchaser's detail design. The purchaser's inspection program should monitor production to assure that design plans are followed to minimize rework. It is important that the purchaser not be put into a position where inadequate fabrication must be accepted because of delivery schedule or any other reason. The purchaser should never accept a defective unit or one where an inordinate amount of rework is necessary. This is best accomplished by assuring: (1) complete purchaser equipment design; (2) qualified fabricator who understands the design; (3) a reasonable plan by the fabricator for successful production of the equipment; (4) qualified fabrication workers; and (5) fabricator quality control to monitor and control production. The purchaser's inspector must ensure that the fabricator has these considerations in order and then monitor results throughout the fabrication and installation activities.

For critical service equipment which must support major loads or which could cause serious loss should failure occur, performance testing is important. This activity assures that the equipment as designed and produced is fit for service. The areas of greatest importance to be checked by this testing activity are the locations of excessive equipment strain and the locations of potential structural failures. Over-strain of the inner corrosion-resistant liner leads ultimately to corrosion failure. Potential structural failures will develop into actual equipment failures after a period of equipment operation. In both cases, visual inspection during the hydrotest of vessels may not have indicated a problem. Hydrotesting alone is not adequate.

General equipment survey techniques are possible both to locate active flaws and to find areas of excessive strain. The basic inspection tools are: (1) Visual inspection; (2) Barcol hardness; (3) lab tests; and (4) equipment tests--(a) brittle coat or photoelastic, (b) strain gauges, and (c) location and analysis of acoustical emission produced by flaw propagation.

In general, these tools can be used together in a simple step-by-step process to identify and locate areas of potential concern. Then the precise nature of the specific problem can be ascertained and repairs specified and eventually rechecked.

The full potential of visual inspection is not completely realized by many inspectors. The specification should allow nothing to be done during fabrication which could reduce the transparency of equipment prior to final inspection. The visual inspection is best performed at night with a 300 to 400 watt spotlight on the opposite side of the wall from the inspector. Generally, the inspector would start on the vessel interior with the light illuminating the equipment wall from the outside. This allows the full wall thickness to be viewed clearly and evaluated rapidly. Defects in joints, flanges, and liners, invisible when viewed by normal lighting, become strikingly apparent using this technique. The visual inspection should be done before and after hydrotesting.

The degree of cure of the inner corrosion-resistant surfaces should also be checked. This can be done by measuring the hardness or by checking the resistance of the liner to attack by solvents, such as acetone. Wall thickness, construction, and strength can likewise be checked by field measurements and lab tests. General mechanical arrangement and dimensions should also be field checked.

If an active flaw develops during hydrotest or during service, or if the wall strains are excessive, these defects must be identified and repaired. Critical flaws may develop and grow very slowly and not be detected during normal hydrotest or even for weeks or months after the equipment is put into service. Likewise, interior liner or structural wall which is excessively strained will deteriorate rapidly when put into service in the presence of a corrosive environment and/or elevated temperature.

These defects can cause premature equipment failure and are probably not detectable using normal techniques during hydrotest. Everything has been done which is humanly possible through design, materials selection, and production inspection to assure quality, but without testing, the above mentioned defects, and potential failure, could still occur.

Through the use of a combination of sensing techniques, equipment can be loaded to design conditions and surveyed for defects. Critical areas of potential failure can be coated to make strain intensity and direction visible. This can be done by photoelastic or brittle coatings. Once maximum strains and orientations of strains are determined, strain gauges can be located to accurately measure peak strain levels in these structural "hot spots." If excessive strains need to be reduced, additional overlay can be prescribed to resolve the problem.

As FRP is strained, it emits sounds. Some sounds are normal and some indicate possible future equipment failure. During hydrotest, a vessel may have acoustic emissions sensors applied directly to its skin to rapidly identify areas of defect and evaluate the potential for failure. These survey test techniques can be used quickly and simply to positively locate structural problems and provide a rational basis for specification of repairs. Often tests results in permanent damage to new vessels. Nondestructive acoustic emission techniques can monitor equipment tests to assure this does not happen.

Once equipment is placed in service, it should be inspected periodically as part of a preventative maintenance program. If equipment problems develop and are discovered through inspection at an early stage, repairs are usually simple. Problems become much more expensive if they are left unattended until equipment failure occurs. Regardless of the care taken during equipment acquisition, problems can develop during operation. These problems are most cost effectively repaired when discovered early.

## SUMMARY

The high corrosion found in the boiler exhaust system is a new and complex challenge to the electric power industry. There are no materials which are clearly the answer to all problems. Fiber Reinforced Plastics provide a material from which much of the equipment in the wet portion of boiler exhaust systems can be constructed.

The advantage of FRP is material performance and corrosion resistance similar to that of metals at a much lower cost. The key is that sulfuric acid concentrations must be kept in a range which FRP can tolerate successfully.

The success of FRP corrosion-resistant equipment depends upon equipment quality. The power plant owner is responsible to assure proper equipment engineering, construction, and maintenance so that high equipment quality is assured. This can be done cost-effectively. The purchaser must take positive engineering action to completely determine and define in detail what the fabricators and contractors must do to produce the desired equipment. The purchaser must use this detailed plan to select the most qualified fabricators and agree upon pricing. The purchaser must carefully monitor production planning and work to assure successful fabrication of the desired process equipment. Finally, the equipment that is to accept major structural loads should be tested to assure that the risk of failure is minimized. This is nothing more than the application of good engineering principles and practices to FRP process equipment and related support structures. Care in engineering procedures will develop high owner confidence in the final FRP process system.

# REFERENCES

1. "Custom Contact Molded Reinforced Polyester Chemical Resistant Process Equipment," NBS Voluntary Product Standard PS 15-69, Washington, D.C., 1969.

2. Pearson, L. E. and A. B. Isham. "Design and Testing of FRP Chemical Storage Tanks," 1966 NACE conference, Miami, Florida.

3. J. Kabelka. "The Behavior of Glass Reinforced Polyester Under Long-Term Stress," Fifth International Reinforced Plastics Conference, London, 1966.

4. Crow, G. L. and H. R. Horsman. "Corrosion in Lime/Limestone Slurry Scrubbers for Coal-Fired Boiler Flue Gases", Corrosion/80 (Paper 274), Chicago, Illinois, March 1980.

5. NACE Corrosion Engineer's Reference Book, National Association of Corrosion Engineers, Houston, Texas, 1980.

6. Guide to Corrosion Resistance of Hetron & Aropol Polyester & Furan Resin Laminates, Bulletin Number 1319-1, Ashland Chemicals, Columbus, Ohio, September 1976.

# FULL-SCALE DAFGD EXPERIENCE AT CENTRAL ILLINOIS PUBLIC SERVICE COMPANY'S NEWTON STATION

By: R. J. Grant, Manager, Environmental Affairs Dept.
J. L. Simpson, Air Quality Engineer
Central Illinois Public Service Company
607 East Adams Street
Springfield, Illinois 62701

## ABSTRACT

The presentation will include a brief history of the Company's Newton Power Station, the selection and design of the dual alkali flue gas desulfurization system and an explanation of the process. The presentation, accompanied by slides, will discuss some of the problems experienced, the materials used in the system, modifications which have been made, operating and maintenance costs, and system performance data.

## COMPANY & STATION BACKGROUND

Central Illinois Public Service Company owns and operates five coal-fired generating stations with a combined capacity of nearly 2200 megawatts. These stations are interconnected in a system-wide network to provide electricity to over 300,000 customers in 551 central and southern Illinois communities. Our primarily rural service area covers more than 20,000 square miles in 65 of Illinois' 102 counties. Illinois' coal reserves, which are second in size only to those of Montana and which account for about 15% of the Nation's total, are highly concentrated within our service area. Increased environmental constraints, primarily sulfur dioxide standards, have required a tremendous effort by CIPS to continue using high sulfur Illinois coal, specifically for boilers defined in the Clean Air Act as "new sources." This is the situation with our newest generating station, Newton Unit No. 1.

Newton Unit 1 is a 595 megawatt, pulverized coal-fired unit which began commercial operation in November of 1977. When the boiler contract was awarded in 1972, CIPS began investigating various scrubbing systems. In August, 1975, CIPS entered into a contract to engineer a Dual Alkali Flue Gas Desulfurization System.

## SELECTION OF DUAL ALKALI SYSTEM

A dual alkali system was selected, in part, because of the relatively poor record of lime/limestone systems in operation at that time. The dual alkali process, backed up by four years of pilot/demonstration and bench scale development, was considered a "second generation" technology and offered several advantages over other processes. Some of these advantages include:

1) Increased reliability of operation
2) Improved utilization of lime
3) Improved $SO_2$ removal efficiency
4) Improved waste handling characteristics
5) Elimination of slurry in the absorber vessel

Construction of this system, the largest of three dual alkali systems now in operation on utility boilers in the United States, began in 1976, but technical and construction problems precluded completion of the system in time to coincide with the commercial startup of the generating unit. The scrubber was placed in service during December of 1979.

During the period between startup of the generating unit and the scrubber, CIPS was granted a variance by the Illinois Pollution Control Board to operate Newton Unit 1 on high sulfur coal without a scrubber. However, in August of 1977, the USEPA issued to CIPS a Notice of Violation of the Clean Air Act, alleging that such operation violated Federal Air Quality Regulations. This matter was settled in December, 1980, when a consent decree between CIPS, USEPA and the Department of Justice was filed.

## SYSTEM DESCRIPTION AS DESIGNED

The dual alkali system for Newton Unit 1 was designed to operate utilizing 4.0% as received sulfur coal with a chloride content of 0.2% by weight. In order to minimize feedstock consumption and to operate successfully with fuel of this quality, the design included several features which set it apart from other systems.

Unlike the other two dual alkali systems, the initial design, which was later modified, included a unique precooler loop, consisting of a chlorobutyl rubber-lined, co-current spray tower and accompanying neutralization system. The purpose of this added loop was to remove the chlorides from the flue gas before scrubbing, thereby reducing feedstock consumption. The precooler inlet is constructed of Hastelloy, and is equipped with tangentially-arranged nozzles called "dentist's bowl" sprays, which keep the area wetted, eliminating wet/dry interface problems. Additional nozzles arranged within the precooler accomplished the gas quenching operation. The resulting solution, which was made up of hydrochloric, sulfuric, and hydrofluoric acids, was quite corrosive, and lead to many problems in the operation of the system. A completely separate neutralization system was included in the precooler loop, and was made up of a thickener where any solids were collected and disposed of with the scrubber wastes; as well as provision for adding lime to the solution for reuse in the system.

The gas flow through the system was as follows: After exiting the boiler, the flue gas passes through electrostatic precipitators where 99.5% of the particulates are removed. The unscrubbed gas was drawn from the precipitators by boiler induced draft fans and four scrubber booster fans, one for each scrubbing train. The gas entered the previously-described precooler, where the gas was quenched from about 350 degrees Fahrenheit to approximately 130 degrees Fahrenheit and any residual fly ash was collected.

The quenched gas, nearly free of chlorides, had left the precooler tower through a rubber-lined transition duct, passed through highly efficient mist eliminators, to the scrubber absorber. These mist eliminators, fabricated of high temperature PVC, helped to prevent carryover of precooler liquor into the sodium loop. This isolation of the two loops was meant to minimize soda ash consumption, and to prevent corrosion of the sodium loop equipment. Although the gas flow through this portion of the system remains the same, one result of some modifications, which will be discussed in more detail later, has been the elimination of the low pH and chloride removal function of the precooler loop and elimination of this first set of mist eliminators.

The scrubber itself was designed as a counterflow mobile-ball tray bed, lined with flakeglass, designed to provide at least 90% $SO_2$ removal. Within the absorber, the gas is contacted by a scrubbing liquor made up of sodium sulfite, sodium carbonate, and sodium hydroxide. The sodium sulfite reacts with $SO_2$ to form sodium bisulfite in this reaction:

$$SO_2 + H_2O + \underset{\text{(Sodium Sulfite)}}{Na_2HSO_3} \dashrightarrow \underset{\text{(Sodium Bisulfite)}}{2NaHSO_3}$$

The scrubbed gas passes through a set of mist eliminators, into flakeglass-lined outlet ducts, where two types of reheat are utilized, and then out the stack.

In order to maintain buffering capability and $SO_2$ removal efficiency, a bleed stream is withdrawn from each operating scrubber and is sent through rubber-lined piping to a battery of three flakeglass-lined reaction tanks, only one of which is now needed, where the solution is mixed with 15% lime slurry. This lime slurry regenerates the sodium bisulfite to sodium sulfite in the reaction:

$$4NaHSO_3 + 2Ca(OH)_2 \rightarrow 2Na_2SO_3 + 3H_2O + 2CaSO_3 \cdot 1/2\ H_2O \downarrow$$

producing a calcium sulfite precipitate. The effluent from the reaction tanks flows to a 100-foot diameter thickener, where the precipitate settles and the clear regenerated liquor overflows to a surge tank for reuse in the system. The thickener has a concrete, conical bottom and carbon steel sidewalls, all lined with precured neoprene rubber.

The calcium sulfite solids are removed from the sodium loop thickeners by progressive cavity, positive displacement pumps, which have natural rubber-lined stators and rotors made of 316 stainless steel. The thickener underflow, at about 35% solids, is pumped first to a filter feed tank and then to a horizontal extractor filter. A fresh water wash is applied to the filtercake in order to recover some of the active sodium present in the filtercake. The washed filtercake is discharged from the filter and mixed with fly ash and lime, using an IUCS stabilization process. The stabilized filtercake is conveyed to a radial stacker area for temporary storage and then is trucked to an on-site landfill for permanent disposal.

## OPERATING EXPERIENCE - FIRST YEAR PROBLEMS

During the first year of operation, numerous problems surfaced, many of which were related to materials of construction.

As previously discussed, the precooler solution was a highly corrosive liquid with a pH below 1.0. Very few materials can operate successfully in such an environment. Rubber-lined piping, used throughout the system worked quite well as long as the lining was not penetrated. However, fiberglass trash grates installed in the bottom of the precooler towers failed, allowing trash as well as the grates themselves to circulate throughout the system. The fiberglass resin used for these grates was not suitable for submersion service and failed for that reason. This lead to chronic failure of the rubber-lined valves and piping throughout the precooler loop. Following this incident, several materials were experimented with to replace failing valves. Stainless steels, 316 and 317, and Incoloy did not hold up long in the precooler environment. Only Hastelloy C-276 provided any extended service.

This problem also contributed to failures of rubber-lined recirculation pumps, when trash in the system penetrated the rubber lining. Trash in the system also caused frequent precooler nozzle pluggage.

On more than one occasion, the PVC mist eliminators which separated the precooler and sodium loops collapsed due to high temperatures. The build-up of solids on temperature sensing probes slowed their response such that temperature excursions brought about by plugged precooler nozzles could not be rapidly detected. The emergency spray system designed to alleviate these occurrences were not triggered in time to prevent meltdown of the mist eliminator panels. System modifications have eliminated the need for these mist eliminators and the other precooler-related corrosion problems.

Expansion joints of teflon fiberglass sandwiched with rubber failed at their corners, which were wire-laced and riveted. Replacement with joints with molded rubber corners alleviated this problem.

The adhesive used to attach the rubber lining in the sodium loop thickener failed, allowing the rubber sheets to unbond and plug the thickener discharge and underflow pump piping. The use of uncoated carbon steel is now under consideration.

Coating and scaling of the ball mills used to slake the lime caused considerable pluggage of the ball mills and required very high maintenance. A new feed system, which utilizes a screw conveyor, preventing contact of the lime and water until both are in the ball mill, eliminated this problem.

Several failures of the flakeglass duct lining have occurred. Most have been attributed to poor application.

MODIFICATIONS

As a result of these problems and others that reduced the availability of the FGD system, CIPS established a scrubber task force/steering committee in an effort to identify and prioritize problem areas and correct them. The efforts of this group have substantially eliminated or reduced nearly all of the major problem areas.

CIPS has applied for a patent to cover many modifications which have been made to the system. These modifications, which include:

1. Changes in system pH;
2. Reaction residence time changes;
3. The use of a single reactor;
4. Changes to the points of lime addition in the system;
5. Altering the agitation and tip speed in the reaction tank; and
6. The use of thickener underflow recycling to the reaction tank

have greatly improved and simplified the operation of the system.

The primary results of these modifications are:

1. The elimination of the low pH precooler solution and the chloride removal function of this loop;

2. The production of much larger crystals in the system, which improve the dewatering characteristics;

3. The production of an essentially non-thixotrophic waste product which is more easily handled and disposed of;

4. Reduced maintenance due to the elimination of the majority of corrosion in the system;

5. Reduced pressure drop across the system allowing full load operation with only three modules instead of four;

6. Reduced operating costs due to simplification of the system;

7. Operating capability, with present contract coal, with only one reaction tank and only one thickener; and

8. Improved availability and reliability of the system.

## SYSTEM AVAILABILITY

The availability of the DAFGD system, as reported to PEDCO during the first eight months of operation, was less than 35%. From August of 1980, when many of the system modifications were instituted, through April, 1982, the system availability exceeded 96%.

## OPERATING AND MAINTENANCE COSTS

Even with the improved reliability which has been experienced, the operation of any scrubber is costly.

### Power Consumption

The DAFGD system consumes about 1.5% of the station gross generation. The cost of this auxiliary power amounted to almost $1.2 million last year. This is less than 0.4 mils/KWH.

### Maintenance Costs

The cost of maintaining the FGD system in 1981 was slightly over $2.1 million, or about 0.7 mils/KWH.

### Feedstock Costs

The FGD system utilizes two primary feedstocks, lime and soda ash. The lime consumption for both the scrubber and filtercake stabilization system runs about 250 tons per day. Soda ash consumption ranges between 18 and 20 tons per day. The cost of these feedstocks in 1981 were nearly $5 million, or about 1.6 mils/KWH.

### Work Force

The operating labor required in the scrubber during 1981 was about $1.3 million. This translates to about 0.4 mils/KWH. Following some recent staff reductions, 36 people are required to operate the scrubber and stabilization facility. This number includes personnel for all four scrubber shifts and an eight-hour/day seven-day/week stabilization operation.

The total annual operation and maintenance costs for the Newton DAFGD system are about $9.5 million or about 3.1 mils/KWH. This cost compares favorably with operating costs of other systems as reported to PEDCO.

## CONCLUSION

Although the number and severity of problems in the FGD system have greatly diminished, CIPS' testing efforts continue, in hopes of further improving system reliability and reduced operating costs.

CIPS' operating experience with the Newton Dual Alkali FGD system, although problematic initially, has been quite satisfactory. The problems present at the outset of operation were virtually eliminated when the double-loop design was abandoned and CIPS' modifications were instituted. The modified system now in operation has performed exceptionally well. System availability, operating and maintenance costs, and $SO_2$ removal efficiency coupled with continuous compliance have all been acceptable, allowing the system to compare favorably, and often exceed, the performance of older FGD systems.

Central Illinois Public Service Company continues to believe in the merits of the "second generation" FGD technology such as the dual alkali system. The system now operating at our Newton facility has demonstrated that problems can be overcome and that the dual-alkali technology does offer improved levels of performance and reliability than that of many of those systems previously available.

# LABORATORY AND FIELD EVALUATION OF MATERIALS FOR FLUE GAS DESULFURIZATION SYSTEMS

By: G. H. Koch and J. A. Beavers
BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

## ABSTRACT

Operating experience in coal-fired power plants has shown that corrosion and degradation of construction materials are major problems in maintaining flue gas desulfurization (FGD) systems. Battelle, in accordance with a request from the Electric Power Research Institute (EPRI), Palo Alto, California, has initiated work to identify the most critical components of FGD systems with respect to corrosion and degradation and to evaluate a wide range of alloys and lining materials for these components utilizing simulated and actual scrubber environments. Previous EPRI-funded work at Battelle aided in the identification of the critical components in FGD systems. This work included a documentation and analysis of utility experience with materials of construction for wet scrubbers, and a survey of the published literature on degradation of materials in FGD systems and in environments that are similar to those encountered in FGD systems.

These data indicated that outlet ducts, stacks, prescrubbers, absorber inlets, and inline reheaters are most prone to materials degradation problems. Accordingly, the laboratory studies were performed under exposure conditions simulating the environments encountered in these components. These studies were carried out in calcium-based solutions with chloride concentrations ranging from 3,000 to 100,000 ppm and pH ranging from 1 to 8. Fluorides also were added to the slurry as calcium fluoride, with a total concentration of 10 percent of the chloride concentration. The laboratory simulations of the outlet duct environments, for duct and reheater evaluations, were accomplished by utilizing a fog spray cabinet in which simulated mist eliminator carryover solutions were atomized. The prescrubber and absorber simulations utilized similar aqueous solutions under submerged conditions.

Results of the laboratory studies indicate the commonly reported trends that alloys are more susceptible to corrosion, both uniform and pitting with increasing chloride concentration, up to 30,000 ppm, decreasing pH, and increasing temperature. Of these three parameters, the effect of pH on the corrosion behavior of the alloys was found to be dominating. However, the results were not nearly as straightforward at higher chloride concentrations. For example, corrosion rates frequently were lower at 100,000 ppm $Cl^-$ than at 30,000 ppm $Cl^-$.

To supplement the laboratory work, field experiments were initiated to evaluate a wide range of alloys and linings in actual scrubber environments. The R. D. Morrow Sr. Power Plant near Hattiesburg, Mississippi, was selected as the site where studies in the mixing zone of the outlet duct will be performed. This region of the scrubber has an extremely aggressive environment because of high chloride and fluoride concentrations, low pH and temperatures ranging from 120-300 F. Specimens of both alloys and linings are being mounted against the duct wall at various locations such that their temperature equilibrates with that of the duct wall. In this way the exposure conditions of the specimens are the same as the duct wall at the specific locations. In addition, a number of condensate collectors are being installed on the duct wall to extract and characterize the flue gas condensate.

## INTRODUCTION

Corrosion and degradation of construction materials are major problems in maintaining flue gas desulfurization (FGD) systems. Acidity and the presence of halides generally have been considered major factors in corrosion failures of FGD components. Moreover, temperature, dew point effects, flue gas velocity, particulates and scale formation have also been found to influence the corrosion behavior.

Battelle's Columbus Laboratories, in accordance with a request from the Electric Power Research Institute (EPRI), Palo Alto, California, has conducted field and literature surveys to identify critical components in FGD systems (1,2,3). This work included documentation and analysis of utility experience with materials of construction for wet scrubbers (1) and a survey of published literature on degradation of materials in FGD systems (2,3). These studies have identified outlet ducts, stacks, prescrubbers, absorber inlets, and inline reheaters as the most critical components with respect to corrosion and degradation. Consequently, an EPRI-Battelle study was initiated to evaluate a range of alloys and linings in simulated outlet duct environments (4,5). Following these studies, the program was expanded to study a wider range of materials in simulated prescrubber, inline reheat and absorber environments.

To supplement the laboratory work, field experiments were started to evaluate alloys and linings in actual scrubber environments. The R. D. Morrow Sr. Power Plant near Hattiesburg, Mississippi, was selected as the site to perform studies in the mixing zone of the outlet duct.

Both laboratory and field experiments are in progress and the results to date are presented below.

## BACKGROUND

A list of components in FGD Systems where serious corrosion and deterioration problems have been encountered as identified in the EPRI-Battelle surveys is given in Table 1. As previously mentioned, the most serious problems have been encountered in the outlet ducts and stacks. Outlet ducts carry wet flue gas at about 50°C (120°F) from the absorber to the stack, or reheated flue gas, depending on the existence and location of a reheater. Also, part of the outlet duct may be exposed to hot flue gas at about 150°C (300°F) during shutdown of the scrubber if bypass reheat is used. Generally, pH values in these ducts are very low because of the absence of the buffering effect of the lime or limestone slurry found elsewhere in the scrubber. In addition, high concentrations of chlorides and fluorides are frequently found in outlet ducts of closed loop FGD systems (6). The combination of low pH, high halide concentrations, and elevated temperatures often results in severe corrosion problems. The least severe environment is in the absorber where relatively mild conditions exist, viz., a pH ranging from 4 to 6 and a constant temperature of about 50°C (120°F).

TABLE 1. MAJOR COMPONENTS AND FAILURE MODES FOR A TYPICAL SCRUBBER. COMPONENTS ARE RANKED ACCORDING TO REPORTED FREQUENCY OF FAILURE

| | Failure Modes | |
|---|---|---|
| Component | Alloys | Linings |
| Ducts (Wet) and Stacks | Pitting<br>Crevice Corrosion | Deterioration<br>Debonding |
| Prescrubber | SCC<br>Pitting<br>Crevice Corrosion<br>Erosion-Corrosion | Deterioration<br>Erosion<br>Debonding |
| Reheater | SCC<br>Pitting<br>Crevice Corrosion | NA* |
| Wet Fan | Pitting<br>Crevice Corrosion<br>Erosion-Corrosion | NA* |
| Absorber | Pitting<br>Crevice Corrosion | Debonding |

*NA = Not applicable.

Table 1 also indicates the predominant failure mode for each component. In alloys, pitting and crevice corrosion were found to occur throughout the FGD system, whereas stress-corrosion cracking (SCC) and erosion-corrosion were confined to specific components. Transgranular SCC has been found with elevated temperatures such as the prescrubber and reheater, and erosion-corrosion was found in areas where high velocities and particulates are encountered.

Over the years a variety of alloys has been used for application in different parts of FGD systems, ranging from carbon steel to nickel-base alloys. Carbon steel was rapidly ruled out as a scrubber construction material because of extremely high corrosion rates. However, under certain severe environmental conditions, such as those that exist in outlet ducts and prescrubbers even highly alloyed iron-base and nickel-base alloys are susceptible to one or more corrosion failure modes.

Susceptibility to each mode of failure of the alloys is critically dependent upon metallurgical as well as environmental conditions. For instance, the more highly alloyed iron- and nickel-base alloys are generally more resistant to pitting and crevice corrosion than the Type 304 or 316 stainless steels (7,8). Molybdenum and, to a lesser degree, chromium impart resistance to pitting and crevice corrosion in austenitic, ferritic and duplex alloys, while nickel improves resistance to transgranular stress-corrosion cracking in austenitic alloys (3,4,8). However, alloy additions are not always beneficial. For example, the ferritic stainless steels which contain little or no nickel are more resistant to transgranular stress-corrosion cracking than are the austenitic alloys, which contain nickel (9,10).

The presence of the tramp impurity carbon and its distribution influences the resistance of austenitic and ferritic stainless steels to intergranular corrosion and intergranular stress-corrosion cracking (11). When in the sensitized condition, the susceptibility to intergranular attack increases with increasing carbon content. Sensitization occurs when the material receives a thermal treatment, such as during welding and stress relieving, that leads to precipitation of chromium carbides at the grain boundaries and a resultant depletion of chromium in the adjacent matrix. The resistance to intergranular attack can be improved by alloy additions such as titanium and niobium which tie up the deleterious carbon (11,12).

Organic and inorganic linings are widely used in FGD systems as cost-effective alternatives to nickel-base alloys. Rubber, vinylester, epoxy, and polyester linings are successfully used in relatively mild environments (1). Most of these linings can withstand severe chemical environments but are vulnerable to temperature excursions, where debonding between the lining and substrate often is observed. Under more severe exposure conditions, actual degradation of the organic linings also occurs. Some fluoroelastomers, vinylesters, and epoxies have been shown to be more resistant to temperature excursions and have been used in outlet ducts and stacks where both severe chemical environments and elevated temperatures are common (1-3,13).

Brick and gunite linings have been used successfully in scrubber components where elevated temperatures and erosive conditions exist such as in stack, outlet ducts, and prescrubbers (1-3). However, in wet stacks, deterioration of mortar has been experienced (14).

## PROGRAM APPROACH

The objective of the program is to evaluate candidate construction materials in a range of simulated and actual FGD environments and identify those materials which are reliable and cost effective in each of these environments. This objective is being pursued through laboratory simulations of field conditions and through field studies. For these evaluations a range of alloys was selected based on their corrosion resistance and cost, the objective being, as mentioned previously, to identify the material that has the best combination of corrosion resistance and cost. The listing of these alloys is shown in Table 2.

TABLE 2. ALLOYS FOR LABORATORY AND FIELD TESTS

| | | | Composition (weight percent) | | | | | |
|---|---|---|---|---|---|---|---|---|
| Alloys | Lab. | Field | Fe | Ni | Cr | Mo | C | Other |
| HASTELLOY®alloy C276 | x | x | 6.0 | Bal. | 16.0 | 16.0 | <.02 | |
| INCONEL®alloy 625 | x | x | 2.5 | Bal. | 21.5 | 9.0 | .05 | |
| HASTELLOY®alloy G3 | | x | 19.5 | Bal. | 22.0 | 7.0 | .015 | Cu5-Cu2 |
| HASTELLOY®alloy G | x | x | 19.5 | Bal. | 22.0 | 6.5 | .05 | Co2.5-Cu2 |
| INCOLOY®alloy 825 | | x | 28.0 | 42.0 | 22.0 | 3.0 | .04 | |
| AL®alloy 6X | x | | Bal. | 24.5 | 21.0 | 6.5 | .03 | Mn2 |
| HUNTINGTON®alloy 904L | x | x | Bal. | 27.0 | 20.0 | 4.5 | .02 | Cu1.5-Mn1.5 |
| JESSOP®alloy JS700 | | x | Bal. | 25.0 | 21.0 | 4.5 | .04 | |
| CARPENTER®alloy 20-6Mo | | x | Bal. | 36.0 | 24.0 | 5.5 | .02 | Cu3 |
| Type 317L4 stainless steel | | x | Bal. | 16.0 | 18.0 | 4.0 | .013 | Mn1.7<br>N 0.14 |
| Type 317LM stainless steel | x | | Bal. | 13.0 | 19.0 | 4.0 | .03 | Mn2-Si1 |
| Type 317L stainless steel | x | | Bal. | 13.0 | 19.0 | 3.0 | .03 | Mn2-Si1 |
| Type 316LM stainless steel | x | | Bal. | 12.0 | 17.0 | 2.75 | .03 | Mn2-Si1 |
| Type 316L stainless steel | x | x | Bal. | 12.0 | 17.0 | 2.0 | .03 | Mn2-Si1 |
| UHB®stainless alloy 44LN | | x | Bal. | 6.0 | 25.0 | 1.5 | .022 | Mn1.7 |
| NU alloy MONIT® | x | x | Bal. | 4.0 | 25.0 | 4.0 | .013 | Ti0.6 |
| FERRALIUM® | x | x | Bal. | 6.0 | 26.0 | 3.0 | .02 | Cu1.7 |
| Titanium alloy Grade 2 | x | x | | | | | .01 | Ti Bal. |
| Titanium alloy Grade 12 | x | x | 0.1 | 0.7 | - | 0.2 | .01 | Ti Bal. |
| ZIRCADYNE®alloy 702 | x | x | 0.12 | 0.05 | 0.10 | - | - | Sn5-Bal.Zr |
| MULTIMET® | x | | Bal. | 20.0 | 21.0 | 3.0 | 0.1 | Mn1.5-Co20 |
| STELLITE®alloy 6B | x | | 3.0 | 3.0 | 30.0 | 1.5 | 1.2 | W4.5-Co Bal. |

® Registered trademarks are shown in the Appendix.

In addition, linings that may be cost effective-alternatives to the alloys are being evaluated in the simulated and actual environments. A list of the linings is given in Tables 3 and 4.

TABLE 3. LININGS FOR LABORATORY EVALUATION

| Linings | Generic |
|---|---|
| FLAKELINE®103 | Glass flake reinforced polyester |
| FLAKELINE 100 | Glass flake reinforced vinylester |
| FLAKELINE 180 | Glass flake reinforced vinylester |
| PLASITE®4004-5 | Vinylester |
| PLASITE 4005 | Vinylester |
| 871X® | Vinylester/fluoroelastomer |
| CXL 2000® | Fluoroelastomer |
| GOODYEAR®LS 551 | Natural rubber |
| GOODYEAR LS 575 | Neoprene rubber |
| CON/CHEM®AR Type 2 | Epoxy phenolic |
| CON/CHEM AR Type 4 | Thermoplastic polyimide |
| CARBOLINE®LS 500-1 | Phenolic |
| SDX®Gunite | Chemically bonded cement |
| PENNGUARD®Glass Block | Glass block |
| HETRON®197-3 | Fiber glass reinforced polyester |

TABLE 4. LININGS FOR EVALUATION IN OUTLET DUCT

| Linings | Generic |
|---|---|
| CXL 2000 | Fluoroelastomer |
| 871X | Vinylester with fluoroelastomer topcoat |
| 282X | Vinylester |
| CON/CHEM AR Type 4 | Modified thermoplastic polyimide |
| DUROMAR®400 HPL | Modified epoxy |
| RESISTALINE®4288 | Fiber glass reinforced polyester |
| SAUEREISEN®72 | Silicate-based gunite |
| PENNGUARD Glass Block | Glass block |

In a previous EPRI-Battelle study, the corrosion behavior of materials in simulated outlet duct environments was evaluated. The results of this study are presented elsewhere (4,5). In the present program, the corrosion behavior of candidate materials is being evaluated in the following scrubber components: prescrubber, reheater, and outlet duct. In all of these studies, the key to success is accurate simulation of the conditions that are encountered in actual scrubbers. This includes the corrosive aqueous environment, temperature, and degree of wetness (immersed or wet gas). The approach of this program was to identify critical species found in FGD systems such as calcium, magnesium, sulfate, chlorides and fluorides, and variables such as pH and temperature, and apply these to the laboratory studies. The laboratory test environments were calcium based since it is suspected that the insoluble deposits such as $CaSO_4$ and $CaF_2$ which are found in actual scrubbers significantly influence failure of the material. Chlorides and, more recently, fluorides have been found to be present in FGD systems. Although the exact role of halides in materials deterioration is not fully understood, it is suspected that certain combinations of halides, acid, and temperature will create extremely aggressive conditions. Therefore, in the present laboratory studies, alloy and lining specimens are being exposed to various combinations of halide concentration, pH, and temperature that are considered to be representative of different sections in scrubber components such as outlet ducts, prescrubbers, and absorbers.

In the field study, it was again attempted to subject the test materials, alloys, and linings to the actual conditions that are thought to be responsible for material failure. It was recognized that in outlet ducts, temperature gradients across the wall, the so-called cold-wall effect, result in conditions detrimental to both alloys and linings. For instance, a very aggressive condensate can form on the wall, due to the cold-wall effect. Therefore, in the present field test, both alloys and linings were mounted against the duct wall such that they would assume the wall temperature and be subjected to similar conditions.

## EXPERIMENTAL PROCEDURES

The following sections describe the experimental procedures for the laboratory and field evaluations.

### LABORATORY EVALUATION

### Specimen Preparation

One-inch square coupons and welded U-bend specimens are being used for the alloy evaluations. The U-bends which contained welds across the apex are stressed according to ASTM Standard Recommended Practice ASTM G 30-79 by means of Type 316 stainless steel bolts that are electrically isolated from the specimens.

The linings are supplied by the vendors in the form of fully coated, unstressed, carbon steel panels. Grooves, 0.1 inch (2.5 mm) in width are machined in the linings to study adhesive properties of the lining. Details of specimen preparation for both alloys and linings are described elsewhere (4,5).

### Solution Preparation

Based on the composition of the actual scrubber environments, the test solutions contain Ca, Mg, Na, $SO_4$, $CO_2$, $N_2$, Cl and F. The chlorides are added as $CaCl_2$ and $MgCl_2$ such that the ratio of calcium and magnesium is 2:1. Sodium is added as NaF up to a concentration of 200 ppm. Additional fluorides are added as $CaF_2$ where the total fluoride concentration is kept as 10 percent of the chloride concentration. After addition of $CaCl_2$ and $MgCl_2$ to demineralize water, the pH is adjusted to the desired value by adding $H_2SO_4$. Then the fluorides are added.

## TESTING PROCEDURES

The laboratory studies are divided into three different groups:

- Immersion tests where alloy and lining specimens are immersed in simulated prescrubber and absorber environments
- Reheat tests where alloy specimens are exposed to simulated outlet duct environments while being subjected to heat exchanger conditions
- Cyclic loading tests where alloy specimens are being subjected to cyclic loads to simulate temperature-induced stresses.

### Immersion Tests

Alloy specimens, coupons and welded U-bends, and lining specimens are being immersed in simulated prescrubber and absorber environments. Table 5 shows the different environments in which the materials are being tested. The temperature of the solutions is being held at near boiling (200 F) and 130 F.

TABLE 5. COMPOSITION OF IMMERSION, REHEAT AND CYCLIC LOAD TEST ENVIRONMENTS

| | | Immersion | Reheat | Cyclic |
|---|---|---|---|---|
| 100,000 ppm [$Cl^-$], | pH 1, 200 F | x | | x |
| | pH 1, 130 F | x | | |
| | pH 4, 200 F | x | | x |
| | pH 4, 130 F | x | | |
| | pH 6, 130 F | x | | |
| | pH 8, 130 F | x | | |
| 30,000 ppm [$Cl^-$], | pH 1, 200 F | x | | |
| | pH 1, 130 F | x | x | |
| | pH 4, 200 F | x | | |
| | pH 4, 130 F | x | x | |
| | pH 6, 130 F | x | | |
| 10,000 ppm [$Cl^-$], | pH 1, 200 F | x | | x |
| | pH 1, 130 F | x | | |
| | pH 4, 200 F | x | | |
| | pH 4, 130 F | x | | x |
| 3,000 ppm [$Cl^-$], | pH 1, 200 F | x | | x |
| | pH 1, 130 F | x | x | |
| | pH 4, 130 F | | x | |

Further, the solutions are partially aerated by maintaining a blanket of an appropriate mixture of air and nitrogen gas (∿ 10 percent $O_2$) over the solutions. Periodically (after 1, 2, 4, 8, and 12 weeks) coupons of each alloy are being removed from the test environments to study the pitting and uniform corrosion rates as a function of exposure time. The U-bend and lining specimens are being exposed to the environments for a total time of 12 weeks.

## Reheat Tests

Alloy specimens, under reheat conditions, are being exposed to a simulated outlet duct environment. Welded U-bend specimens are being clamped onto tubular racks through which steam is passed. The racks, which are fabricated of Titanium Grade 12, are electrically isolated from the specimens by means of TEFLON® tape which prevents galvanic effects but minimizes thermal insulation of the racks from the specimens. The racks containing the U-bend specimens are suspended in simulated outlet duct environments produced by a makeup solution in a modified fog cabinet. Details of outlet duct environment simulation are described elsewhere (4,5). The chloride concentrations of the makeup solutions are 3,000 and 30,000 ppm and the pH is 1 and 4 (see Table 5).

During exposure to the wet gas, the steam temperature of one test rack is maintained at 250 F. To simulate shutdown conditions, the temperature of a second test rack is alternated between 120 F and 250 F, i.e., 2 hours per 24 hours at 120 F. After 6-weeks' exposure, the specimens are removed, weighed, and examined for localized attack.

## Cyclic Load Testing

Cyclic load testing is being performed to simulate the stresses that result from temperature fluctuation encountered during startup and shutdown of a scrubber. Cylindrical specimens, having a 1/8-inch (3.2 mm) diameter and containing a weld in the middle, are cyclic loaded in the test solutions shown in Table 5, at a temperature of 200 F. Initially, welded Type 316L stainless steel specimens are being cyclically loaded between about 30 and 70 percent of the 0.2 offset yield strength according to a trapezodial wave form.

The holding period at the upper and lower loads is held constant at 25 minutes while the ramp period between the two loads is varied from 2.5 minutes to 25 minutes*. These loading rates corresponded to effective strain rates, based on the stress strain curves for the specimens of approximately $1.1\times10^{-6}$ in./$_{\text{in-sec}}$ to $5.5\times10^{-7}$ in./$_{\text{in-sec}}$.

## FIELD EVALUATION

To supplement the laboratory work, field experiments are being carried out to evaluate a range of alloys and linings in actual scrubber environments (see Tables 2 and 4). The R. D. Morrow, Sr., plant near Hattiesburg, Mississippi, was selected as the site where studies in the mixing zone of the outlet duct would be performed. In the outlet duct of the Unit 2 scrubber, welded** and unwelded** samples (6 in. x 6 in.) are being mounted directly to the duct wall, at various locations, such that their temperature equilibrates with that of the duct wall. In this way the exposure conditions of the specimens are very similar to the duct wall at the specific locations. For comparison purposes, additional alloy specimens are being mounted on spools in the flue gas stream.

---

*The time period for the increasing load ramp always is the same as the time period for the decreasing load ramp.

**Both welded and unwelded specimens were supplied by the alloy manufacturers.

In addition to the alloy exposure tests, condensate collectors are being installed on the wall (Figure 1). Using these collectors, flue gas condensate which forms on specific sites of the wall can be extracted and analyzed. Further, the collectors contain thermocouples and wetness gauges so that the temperature and degree of wetness can be measured.

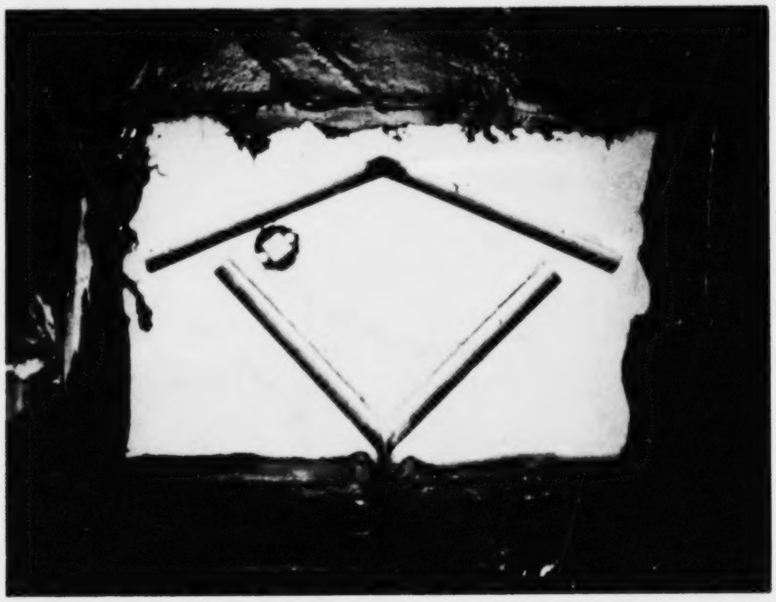


Figure 1. Photograph showing a condensate collector mounted on the inside of the outlet duct of the R. D. Morrow, Sr., power plant. Condensate is collected at bottom. The thermocouple is located in the upper right and the wetness gauge is located in the upper left.

In the outlet duct of the Unit 1 scrubber, eight different linings are being installed (Table 4). Before lining application, carbon steel plates are being installed on the inside of the outlet duct to provide a virgin substrate for application of the linings. Surface treatment and lining application is being performed according to the applicator's specifications.

The maximum testing time for both alloys and linings will be one year. After one year of exposure, the alloy specimens will be removed and studied for uniform corrosion and localized attack, e.g, pitting, crevice corrosion, intergranular attack, stress-corrosion cracking. Periodic visual inspection will be performed on the linings.

## RESULTS

In this Section, some preliminary results of the materials evaluation are presented.

### LABORATORY EVALUATION

#### Immersion Tests

Figure 2 shows an example of cumulative loss in thickness calculated from the weight-loss of some typical nickel- and iron-base alloys in a simulated prescrubber environment having a chloride concentration of 100,000 ppm, pH 1, and a temperature of 200 F. The alloys exposed to this environment can be divided into three different general groups according to their apparent corrosion behavior: A, B, and C. In Group A, which contains HASTELLOY Alloy C-276, Titanium Grade 2, Titanium Grade 12, and AL6X, the gradual slope of the

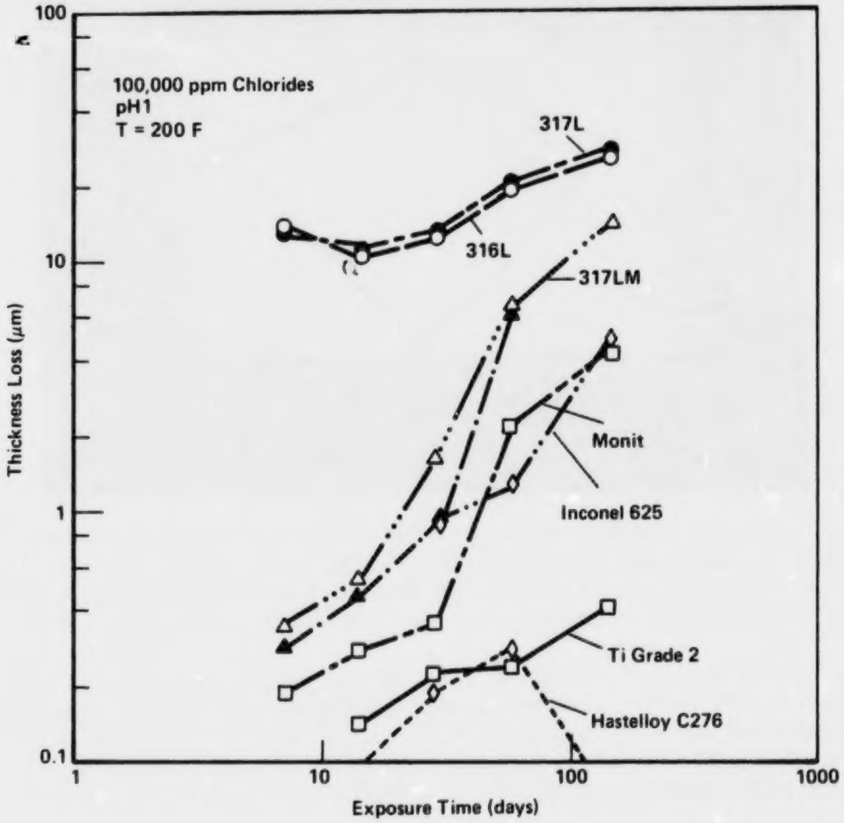


Figure 2. Diagram showing thickness-loss of selected alloys as a function exposure time in a simulated scrubber solution containing 100,000 ppm chlorides, at pH 1, and a temperature of 200 F.

thickness-loss line suggests the presence of protective films during exposure to this environment. On the other hand, the steep increase in weight-loss of the Group B alloys which contain INCONEL Alloy 625, HASTELLOY Alloy G, Alloy 904 L, Type 317LM stainless steel, MONIT, FERRALIUM, and MULTIMET suggests that no film was present or that an initial protective film was breached at an early stage after which rapid attack occurred. In Group C, Type 317L, 316LM, and 316L stainless steels, and STELLITE 6B, the initial corrosion rate was high. However, the rate of corrosion decreased with time, possibly due to the formation of a protective surface film during exposure. Indeed, examination of the specimens indicated a tenacious black film had formed on these alloys after a short period of exposure. X-ray diffraction analysis of the film formed on Type 316L stainless steel indicated the presence of $Fe_2O_3$ and $CaF_2$.

The influence of solution composition on thickness-loss of selected alloys is shown in Figure 3. These data show that the rate of attack was highest at intermediate chloride concentrations for all of the alloys examined. In particular, Titanium Grade 2 and Zirconium corroded very rapidly in the intermediate environments; after one week, the test samples had almost completely dissolved. Figure 4 shows the corrosion behavior of some alloys in a 10,000 ppm chloride, pH 1, 200 F solution. The slopes of the curves are similar to those of Group B in Figure 2, indicating rapid uniform attack. One exception was AL6X whose thickness-loss after an initially sharp increase remained constant. Again, under these low pH high-temperature conditions, the corrosion rates of titanium and zirconium were very high. On the other hand, the rates of attack of the ferritic alloy MONIT and the duplex alloy FERRALIUM were very small.

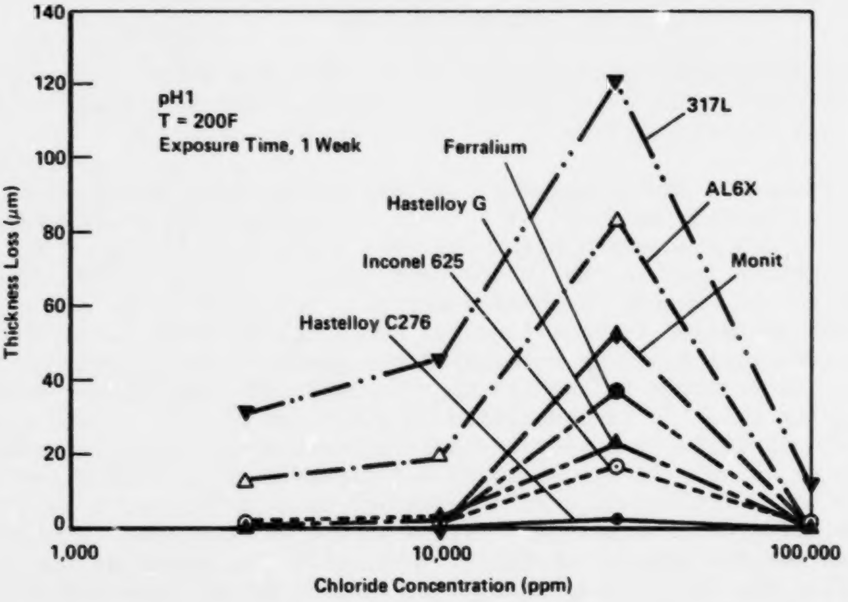


Figure 3. Diagram showing thickness-loss of selected alloys as a function of chloride concentration in pH 1, 200 F solutions.

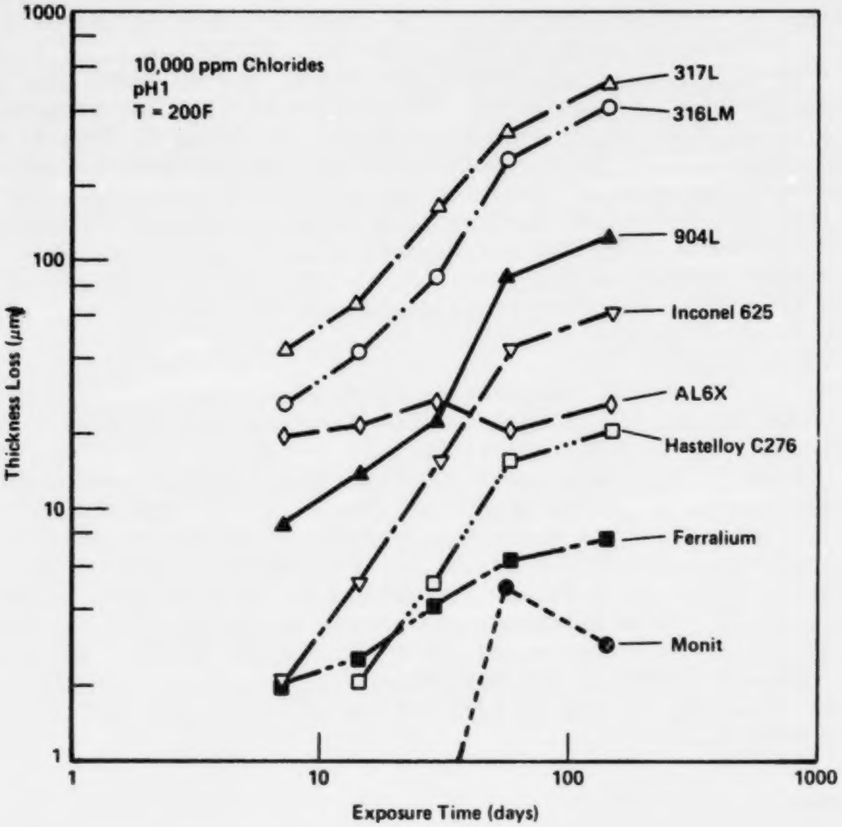


Figure 4. Diagram showing thickness-loss of selected alloys as a function of exposure time in a simulated scrubber solution containing 10,000 ppm chlorides, at pH 1 and a temperature of 200 F.

Since zirconium and titanium alloys are known to be susceptible to fluoride attack, a fluoride analysis of some test solutions was performed. Analysis of a pH 1, 200 F solution after one week's exposure indicated the presence of 35 ppm fluoride ions in the 100,000 ppm chloride solution and 700 ppm fluoride in the 30,000 ppm chloride solution. Subsequent work has shown that this peculiar variation in free fluoride concentration with variation in chloride concentration may be related to the activity coefficient of the hydrogen ion. As reported in the literature (15), this coefficient decreases with increasing chloride concentration to a minimum of 0.75 around a chloride concentration of 10,000 ppm at room temperature and increases thereafter to values as high as 40. Thus, one would anticipate that at high chloride concentrations very little $H_2SO_4$ would be needed to achieve a pH 1 as compared to lower chloride concentrations. This behavior was observed in preparation of solutions for the present studies. Apparently the amount of free fluoride liberated from the $CaF_2$ precipitate is a function of the quantity of $H_2SO_4$ added rather than the pH.

Further evaluation of the alloys at higher pH values (4, 6, and 8) and lower temperature (130 F) showed considerable decrease in corrosion attack as illustrated for some alloys in Tables 6 and 7.

TABLE 6. THICKNESS-LOSS OF SOME ALLOYS AFTER ONE WEEK'S EXPOSURE IN 30,000 ppm CHLORIDE, 200 F ENVIRONMENT AT pH 1 AND 4

| Alloys | Thickness Loss (μm) pH 1 | Thickness Loss (μm) pH 4 |
|---|---|---|
| INCONEL alloy 625 | 16.93 | 0.01 |
| HASTELLOY alloy G | 22.3 | - |
| Alloy 904L | 24.79 | 0.05 |
| Type 316L stainless steel | 70.37 | 0.03 |
| FERRALIUM | 37.95 | 0.01 |
| TITANIUM alloy Grade 2 | > 1900.0 | 0.05 |

TABLE 7. THICKNESS-LOSS OF SOME ALLOYS AFTER ONE WEEK'S EXPOSURE IN 30,000 ppm CHLORIDE, pH 1 ENVIRONMENT AT 200 F AND 130 F

| Alloys | Thickness Loss (μm) 200 F | Thickness Loss (μm) 130 F |
|---|---|---|
| INCONEL alloy 625 | 16.93 | 0.15 |
| HASTELLOY alloy G | 22.3 | 0.19 |
| Alloy 904L | 24.79 | 7.67 |
| Type 316L stainless steel | 70.37 | 0.01 |
| FERRALIUM | 37.95 | - |
| TITANIUM alloy Grade 2 | > 1900.0 | 35.32 |

The mode of attack of the alloys also was a function of solution composition. In general, pitting was most severe at the low pHs and high temperatures. However, under these severe conditions, pitting was not found where rapid rates of uniform attack occurred.

In addition to the weight-loss coupons, welded U-bends were exposed to the simulated scrubber environments for 12 weeks to study susceptibility to localized attack such as stress-corrosion cracking and intergranular corrosion. A systematic evaluation of the U-bends has not yet been completed.

Grooved lining specimens also were exposed to the test environments for 12 weeks. Although, to date, no sampling of the resistance of these linings has been made, it was found that all the linings showed a decrease in hardness and some degree of debonding after exposure to the pH 1 environments. At the high pH values, generally no debonding was observed. From observation of the failure morphology, it appears that in the less corrosive environments (100,000 ppm $Cl^-$) debonding occurred prior to corrosion of the carbon steel substrate whereas, in the more corrosive environment (30,000 and 10,000 ppm $Cl^-$), corrosion products were present at the tip of the lining-substrate interface.

## Reheat Tests

Exposure tests were performed on U-bend specimens in simulated reheater environments at approximately 130 F and at chloride concentrations of 3,000 and 30,000 ppm. After exposure, the U-bends were weighed and studied for localized attack. In most cases, in particular in the 3000 ppm chloride pH 1 mist, a thick scale formed on the apex of the U-bends exposed either continuously or alternately at 250 F. After removal of the scale, severe uniform or crevice attack was found. At places where no scale had formed, viz., the sides of the U-bend, no attack was observed. It can be speculated that $H_2SO_4$ concentrated in the scale on both the continuously and alternately heated U-bends. At these concentrations the temperature (250 F) of the reheater tube was below the acid dew point. Thus, all specimens may have been continuously exposed to a very concentrated acid.

## Cyclic Loading Tests

Initial cyclic loading tests indicated that Type 316L stainless steel is susceptible to transgranular stress-corrosion cracking in a 100,000 ppm chloride, pH 1, 200 F solution over a range of effective strain rates from $5.5 \times 10^{-7}$ to $1.1 \times 10^{-6}$ in/in-sec. The shortest time to failure was found at the lowest effective strain rates examined. Transgranular SCC was found in the weld, heat-affected zone, and base material (Figure 5).

## DISCUSSION

Based upon the preliminary results described above, it is evident that chlorides and fluorides in conjunction with low pH and high temperature play a significant role in corrosion of the candidate alloys. It can be speculated that certain conditions, viz., high acid concentration and high temperature, favor partial dissociation of $CaF_2$ forming free fluoride ions and subsequently hydrofluoric acid, which in small quantities is known to be detrimental to nickel- and iron-base alloys and, in particular, to titanium and zirconium alloys. The presence of chloride ions and crevice environments created by the scale may enhance corrosion attack.

The combination of high chloride/fluoride, low pH and high temperature also appeared to be detrimental to organic and inorganic linings. Deterioration of the linings and debonding were common under these conditions. As in the case of alloys, deterioration of the linings was less at higher pH values and lower temperatures.

Although the environments in which exposure tests were performed were simulated or artificial, some significant similarities exist between these artificial and actual scrubber environments. For instance, scale which forms on outlet duct walls have been found to contain high concentrations of fluoride present as $CaF_2$. Further, in closed loop systems, the chloride concentration of the condensate from the duct wall is high and the pH is low. Chloride concentrations of 30,000 ppm and pH values near 1 have been measured. Moreover, in outlet ducts in which bypass reheats are used, temperatures of 300 F are not uncommon. Thus it appears that the laboratory environments used in the present studies have many important factors in common with the actual FGD environments.

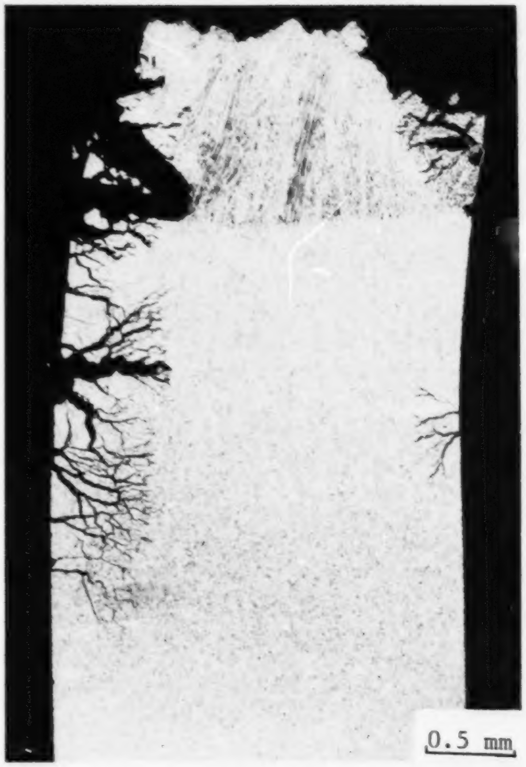


Figure 5. Optical micrograph of a cross section of Type 316 stainless steel after cyclic loading (strain rate 5.5 x $10^{-7}$ in./in-sec) 100,000 ppm chloride, pH 1, T = 200 F solution; transgranular stress corrosion cracks can be seen in the weld, heat-affected zone, and base material.

## CONCLUSIONS

Based on the preliminary results, the following conclusions can be drawn:

- The most severe corrosion occurred at intermediate chloride concentration (30,000 ppm) at low pH and high temperature
- The presence of free fluoride may be partially responsible for the severe corrosion observed
- Corrosion rates are much lower at higher pH values and lower temperatures.

## ACKNOWLEDGMENTS

This work is supported by the Electric Power Research Institute, Inc., Palo Alto, California. The authors are indebted to Mr. C. E. Dene and

Dr. B. C. Syrett for their support and guidance during the course of this work. Further, the authors express their appreciation for the support and cooperation of personnel of the South Mississippi Electric Power Association during the field evaluation at the R. D. Morrow, Sr., power plant.

## REFERENCES

1. H. S. Rosenberg, H. H. Krause, L. J. Nowacki, C. W. Kistler, J. A. Beavers, R. J. Dick, and J. H. Oxley, "Construction Materials for Wet Scrubbers", EPRI Report CS-1736, Project 982-14, March 1981.

2. G. H. Koch, J. A. Beavers, N. G. Thompson, and W. E. Berry, "A Survey of the Performance of Candidate Construction Materials for Flue Gas Desulfurization Systems", Project RP 1871-1, to be published by EPRI (1981).

3. J. A. Beavers and G. H. Koch, "Review of Corrosion-Related Failures in Flue Gas Desulfurization Systems", Paper Number 202, Corrosion/82, NACE (1982).

4. G. H. Koch and J. A. Beavers, "The Experimental Evaluation of Alloys and Linings in Simulated Duct Environments for a Lime/Limestone Scrubber", Project RP 1871-1, to be published by EPRI (1981).

5. G. H. Koch and J. A. Beavers, "Experimental Evaluations of Alloys and Linings in Simulated Duct Environments for a Lime/Limestone Scrubber", Paper Number 197, Corrosion/82, NACE (1982).

6. E. R. Dille and T. F. Lemke, "FGD Corrosion at the R. D. Morrow, Sr., Generating Plant. Seminar on Solving Corrosion Problems in Air Pollution Control Equipment", Denver, Colorado (1981) p. 15.

7. S. Sklarska-Smialowska, "The Pitting of Iron-Chromium-Nickel Alloys", Conference on Localized Corrosion, Williamsburg, Virginia (1973) p. 312.

8. A. I. Asphahani, P. E. Manning, W. L. Silence, and T. G. Hodge, "Highly Alloyed Stainless Materials for Seawater Application", Paper Number 29, Corrosion/80, NACE (1980).

9. R. T. Steigerwald, A. P. Bond, H. J. Dundas, and E. A. Lizlovs, "The New Fe-Cr-Mo Ferritic Stainless Steels", Corrosion, Vol. 33:8, 1977, p. 279.

10. A. P. Bond and H. S. Dundas, "Effect of Composition on the Stress-Corrosion Cracking of Stainless Steels", Corrosion, Vol. 24:10, 1968, p. 344.

11. M. Henthorne, "Intergranular Corrosion in Iron and Nickel-Base Alloys", Localized Corrosion - Cause of Metal Failure, ASTM STP 616, 1972, p. 66.

12. A. B. Bond and E. A. Lizlovs, "Intergranular Corrosion of Ferritic Stainless Steels", Journal Electrochemical Society, Vol. 116, 1969, p. 1305.

13. A. L. Hendricks, G. B. Wauters, and W. T. Singleton, "Vinyl Ester Coating for Pollution Control Equipment", Paper Number 41, Corrosion/79, NACE (1979).

14. C. E. Dene, Electric Power Research Institute, Inc., Palo Alto, California. Private Communication, 1982.

15. Kirk-Othmar, Encyclopedia of Chemical Technology, Volume 7.

# APPENDIX

## Registered Trademark of Products Used in This Study

AL is a registered trademark for products of Allegheny Ludlum Corporation.

CARBOLINE is a registered trademark for products of Carboline Corporation.

CARPENTER is a registered trademark for products of Carpenter Technology Corporation.

CON/CHEM is a registered trademark for products of Con/Chem Corporation.

CXL2000 is a registered trademark of Colebrand, Ltd.

DUROMAR is a registered trademark for products of Martek Manufacturing, Inc.

FERRALIUM is a registered trademark of Bonar Langley Alloys, Ltd.

FLAKELINE 871X is a registered trademark of Ceilcote Corporation.

GOODYEAR is a registered trademark for products of the Goodyear Tire and Rubber Corporation.

HASTELLOY, MULTIMET, AND STELLITE are registered trademarks for products of the Cabot Corporation.

HETRON is a registered trademark for products of Ashland Chemical Company.

INCONEL, INCOLOY, AND HUNTINGTON are registered trademarks for products of Huntington Alloys, Inc.

JESSOP is a registered trademark for products of Jessop Steel Company.

PLASITE is a registered trademark for products of Wisconsin Protective Coatings Corporation.

RESISTALINE is a registered trademark for products of Corrosioneering, Inc.

SAUEREISEN is a registered trademark for products of Sauereisen Cement Company.

SDX and PENNGUARD are registered trademarks for products of Pennwalt Corporation.

TEFLON is a registered trademark for duPont deNemours & Company.

# MATERIALS OF CONSTRUCTION PROBLEMS AT PLEASANTS POWER STATION

by: W. R. Cress and T. L. Misner
Allegheny Power Service Corporation
800 Cabin Hill Drive
Greensburg, PA 15601

## ABSTRACT

Since preliminary operations began in 1978, there have been material failures in the ducts and in a chimney liner downstream of the scrubbers at Pleasants Power Station. This is our primary area of concern due to the extended outages that are required to replace these coating systems. In some duct areas we are already experiencing failures of our third attempt at finding materials suitable for this environment. Other material problems such as pumps and piping have been very minor.

This paper summarizes the material behavior experiences at Pleasants after some three years and 20,000 hours of operations.

## INTRODUCTION

Pleasants Power Station is located on the Ohio River some 20 miles upriver from Parkersburg, West Virginia. The station is jointly owned by Monongahela Power Company, The Potomac Edison Company and West Penn Power Company, operating subsidiaries of the Allegheny Power System. Engineering and Construction services for the plant were provided by United Engineers and Constructors. The two nominal 600 Mwe units were placed in service on March 31, 1979 and December 15, 1980, respectively.

In order to comply with particulate emission regulation limits of .05 #/MBtu and sulfur dioxide limits of 1.2 #/MBtu, the plant was provided with electrostatic precipitators designed for 99.55% efficiency and with wet lime scrubbers designed for 90% efficiency. Induced draft fans follow each units two precipitators and discharge into a common plenum. From here, four $SO_2$ booster fans take suction and each discharges through its own scrubber. Full load compliance capability is achievable with one scrubber out of service.

Two ducts allow gas from the plenum to bypass the scrubbers and recombine with the scrubbed gas prior to entering the stack. This open bypass design is considered necessary in order to: (1) provide reheat sufficient to dry the chimney walls and thus prevent windstripping and discharge of moisture droplets, and (2) minimize the probability of ductwork implosion that can occur due to pressure transients resulting from damper or fan failures.

## MATERIAL PROBLEM AREAS

The major material problem at the Pleasants Power Station has been the coatings in the scrubber, the outlet ductwork and the chimney. Replacement of the expansion joints in the outlet ducting has also been necessary. It is these subject areas that will be primarily addressed in this report.

In evaluating materials problems at our plant one should note that this is a high sulfur coal scrubber with a continuous hot gas bypass. Thus, our duct/stack experiences do not necessarily apply to low sulfur coal scrubbers or to plants that do not have gas bypassing.

### CHIMNEY LINER

The plant has a 1000 ft. concrete stack for each unit. Each of these was to contain a 20 ft. diameter carbon steel flue suitably coated to resist acid.

With a bypass duct it would be necessary to find a coating material capable of withstanding corrosion as well as temperatures over 300°F. In 1973 no high sulfur coal scrubbers were in existence with this severe an operating condition and, thus, proven materials were not available. Decision was made to defer commitment of the coating material to the latest possible time in the construction schedule. As well as watching developments in the industry, we began material tests in an operating chimney. These included a vinylester coating, a fluoroelastomer coating, a non-asphaltic mastic coating, and a polyester coating. Only the vinylester and the fluoroelastomer survived this 300°F service condition. These two materials also performed successfully for many months in a pilot plant scrubber that we were testing.

By the time bids for these two materials were received in February 1978, several FGD systems using vinylester were operating satisfactorily with exposure times of two to three years. Evaluation of the coating offerings recommended use of vinylester. The application of this coating to Unit No. 1 liner was completed in late summer of 1978.

Within a few weeks after initial operation of this unit it was found that some 12% of this coating had disbonded and fallen off. This failure was attributed to overthickness of the coating.

At this time, a complete reevaluation was made for Unit No. 2 chimney liner system. It was decided that time was available to replace Unit No. 2 steel liner with an acid resistant brick liner prior to initial start-up.

This brick replacement option was not viable for Unit No. 1 due to the very long outage that would have been necessary. Therefore, a three-month outage was taken in mid-1979 to replace the Unit No. 1 vinylester coating. This recoating is performing satisfactorily after 2-1/2 years exposure with the exception of some disbonding that has recently occurred on the roof of the scrubber outlet ducts. Several operating practices have been instituted in an attempt to prolong the life of the vinylester:

(1) Far more careful control of application procedures and coating thickness was exercised during the 1979 recoating.

(2) Exposure to temperatures in excess of 170°F has been avoided when possible even during start-up and shut-down procedures.

(3) Exposure to extremely cold ambient temperatures ($< 30°F$) has been avoided during winter outages. This is primarily done by keeping the glycol air preheating coils in service during an outage.

(Having observed that a number of vinylester coating bonding failures at various utilities occurred coincident with cold weather outages, we undertook a series of laboratory tests to examine this effect. These tests indicated a propensity to bonding failures with thermal cycling and exposure to temperatures below freezing.)

In reviewing the histories of other installations, we note that failures of vinylesters have typically occurred after some two to four years. Thus, we will not know for several more years if the operational precautions that have been instituted will be successful in prolonging the life of this material. Our review of operating histories of other high sulfur coal scrubbers with hot gas bypass has failed to find any other types of coatings with equivalent exposure times. Thus, it is also too early to know if more durable coatings exist.

Inspection of the Unit No. 2 brick liner after its first year of operation showed it to be in satisfactory condition except for two major cracks which do not appear to threaten the structural integrity of the liner. Other utilities are experiencing softening of mortar in wet gas service. We have conducted gas flow modeling and installed baffling to obtain more rapid mixing of the wet gas and hot gas bypass within the ductwork. Hopefully this will prevent entry of wet gas into the brick chimney and prolong its life.

Chimney durability continues to be our area of greatest concern due to the cost of the extensive outages necessary for repairs.

## DUCT COATINGS

On Unit No. 1, the outlet ductwork had originally been coated with vinylester which failed during the initial operation of the plant. Therefore, concurrent with the relining of the stack, the wet gas duct zone downstream of each scrubber was recoated with vinylester. In an attempt to find a more durable material, four different gunite type coatings were used to recoat the ductwork from the bypass duct junction to the chimney entry.

During the period from September 1979 to August 1980 these materials had deteriorated to the point where replacement was again necessary:

(1) Aluminum silicate cement: Significant erosion. Practically nonexistent on the bottom of the duct.

(2) Sodium silicate cement: Appeared soft and spongy. Porosity permitted acid attack of the duct steel.

(3) Calcium silicate cement: Significant erosion. Wire mesh was exposed in approximately one third of the area.

(4) Chemically cured colloidal silica cement: Extensive cracking. Material remained hard but acid had attacked the carbon steel duct beneath it.

During the same eleven months, coupons of various alloy metals were tested. These tests indicated that only those alloys with more than some 9% Molybdenum had prospects for plant lifetime survival in the corrosive conditions in the wet gases exiting the scrubbers. Once these wet gases were mixed with the bypass gas stream, only an alloy with some 16% Molybdenum indicated a reasonable chance for survival.

An alloy UNS N08825 dust shield over an expansion joint in the bypass gas "mixing zone" showed severe pitting attack in a zone 5 to 10 ft. above the duct floor. This indicated that our "bypass mixing zone" test coupons which were near the floor had not been exposed to the most severe condition. Alloy test coupon racks are now in place in the more severe location. We are also testing samples of titanium and a high temperature epoxy.

In addition, during this same eleven-month period, several systems were tested using small test panels:

(1) Potassium silicate cement.

(2) Potassium silicate cement over an asphalt-urethane membrane.

(3) A mixture of potassium silicate cement and hydraulic cement over an asphalt-urethane membrane.

(4) Borosilicate glass block over an asphalt-urethane membrane.

Conclusions from these test panels and the duct installations were:

(1) The borosilicate glass block, with no deterioration occurring in six months, showed promise.

(2) Hydraulic or calcium cements did not hold up well and should not be used in this service.

(3) Ducts must be coated with an acid resistant membrane under the gunite.

(4) Potassium silicate cement remained hard and in good condition.

Following this, duct coatings for both units were installed in mid-1980:

(1) The mixing zones of the Unit No. 1 ducts and the east duct of Unit No. 2 were coated with potassium silicate cement over a vinylester membrane.

(2) The west duct of Unit No. 2 was coated with chemically cured colloidal silica cement over a vinylester membrane. A coating of vinylester was also placed over the cement.

(3) A test section of sodium silicate cement over vinylester was installed at the east duct breeching entry on Unit No. 2.

(4) A test section of borosilicate glass block was installed in the wet gas zone exiting module 2D.

Late in 1981 an additional test section of borosilicate glass block was installed in the west breeching entry of the Unit No. 1 stack where the material could be evaluated under mixing zone conditions.

During the most recent inspection of these units in April 1982, the following conditions were noted:

(1) Except for a two square foot failure, the potassium silicate cement remained hard with crack lines every several feet. The vinylester membrane was in good condition.

(2) The chemically cured colloidal silica cement had failed in some areas. The wire mesh reinforcing was badly attacked and no longer existed in some areas.

(3) The borosilicate glass block was in good condition.

(4) The vinylester coating in the module wet gas outlet ducts was in good condition after some 2-1/2 years except for some areas on the duct roofs where disbondment had occurred due to excessive coating thickness.

(5) The vinylester coating on the Unit No. 1 chimney remained in good condition after some 2-1/2 years exposure.

(6) The brick chimney liner on Unit No. 2 was in good condition after some 16 months service.

## ABSORBER VESSEL AND RECIRCULATION TANK LININGS

All of the absorber vessels and recycle tanks on both units were lined with natural rubber. During August 1980, an inspection of the Unit No. 1 scrubbers revealed many blisters of up to 1" diameter. These were water blisters that had formed between the steel and the rubber. No appreciable corrosion occurred. The blisters in the recirculation tanks were more frequent and larger in diameter.

As Unit No. 2 was lined but not yet in operation, additional efforts were made to cure the rubber linings before initial service. However, following its initial year of service, Unit No. 2 also showed blistering.

The blisters have continued to grow with some in the Unit No. 1 recycle tank approaching the size of baseballs after three years' service. The steel is still sound.

An absorber and several recycle tanks on Unit No. 1 were relined with chlorobutyl rubber to obtain less permeability. In somewhat less than one year's service, these liners have not shown blistering.

A small test tank lined with various types of rubber provides both insulated and uninsulated wall sections and is partially filled with liquor to evaluate emersion effects. The only rubber in this test tank to show blistering is the same type of natural rubber provided for our scrubbers. This blistering section had been deliberately undercured and is on an uninsulated wall.

## EXPANSION JOINTS

The original duct design specified fabric expansion joints. These joints were not liquid tight and a continuous leaking of acid resulted. All joints downstream of the scrubbers were replaced during the summer of 1980 with reinforced (stainless steel and fiberglass) fluoroelastomer. These new joints have provided good service to date. Since these joints will fill with liquid, drains have been added to each expansion joint.

The initial fabric expansion joints downstream of the scrubber had been selected in order to withstand the high temperature that would occur with a stalled air heater occurring when all scrubbers were bypassed. In order to obtain better material durability, we have accepted a lower temperature material. The scrubbers have performed reliably enough that this risk is acceptably low.

Extensive corrosion was found at flanged connections in the ductwork downstream of the scrubbers. Coatings are not easily applied to flanges and the sharp corners are easily attacked. When corrosion occurs under the coating, it destroys the steel and disbonds protective materials. Field tests indicated that the flanges should be made of UNS N06625 alloy. The details require special attention with the alloy extending under the coating system.

## PUMPS

Only the lime slurry pumps have caused repetitive problems. A pump liner wear problem was corrected by reducing pump speed. If the percent sulfur in the coal were to increase from the current level of 3% to the design level of 4.5%, then lime slurry pump replacement may be necessary to restore its capacity. All other rubber lined pumps have performed reasonably considering the service. Only some 50% of the pumps have required relining in some 20,000 service hours.

## PIPING

Rubber lined piping has performed reasonably well thus far. The only consistent problem has been repeated replacements of a 16" elbow downstream of the hydroclone in the quench water system. A cavitation effect caused by the hydroclone is the suspected cause.

The 316L stainless steel piping located above the mist eliminator shows severe pitting attack. Being beyond the mist eliminator, this piping is in a low pH area.

## ISOLATION DAMPERS

The 317L isolation dampers on the module outlets have begun to show pitting attack. This wet duct area is free of any deposits but, of course, has low pH.

## VALVES

The only process valves used for throttling service are the lime feed control valves. The original knife gate "V" port control valves had continuing packing leakage problems. These were replaced after 1-1/2 years with diaphragm valves. The replacements are operating satisfactorily after 1-1/2 years.

## TANKS

(1) The coal tar epoxy on the thickener has required patching.

(2) The carbon steel thickener overflow tank was pitting and was, therefore, coated with coal tar epoxy.

(3) The carbon steel lime slurry tank is pitting under "barnacle" type encrustations that form on the walls. No corrective action has yet been instituted other than removal of the "barnacles" during tank cleanings.

## CONCLUSIONS

Considerable effort was exerted during the specification and design stages of the Pleasants scrubbing facility to ascertain as much information as possible concerning the successes and failures of materials at other utilities. During the 1973-76 time frame, more frequently than not the experiences of other utilities warned of problems to avoid but did not always provide proven solutions.

Unfortunately, proven solutions were not available regarding materials suitability in scrubbers, outlet ducting and chimneys. We were well aware of this and deliberately forestalled commitment to materials in this area to the latest point in time commensurate with our construction schedule.

In this materials problem area of the ducts and chimneys, other than identifying some disasters to avoid, the industry does not know much more today than it did 5 or 10 years ago. We, as an industry, have still not seen proven performance in excess of a few years in this hostile environment of the bypass mixing zone of high sulfur coal scrubbers.

The electric utility industry is beginning to realize that there is probably no "good" solution to be found for ducts and chimneys downstream of scrubbers--only a "least worst" choice. Hopefully, in the coming years the industry will "prove out" the materials of construction which will provide reasonable service lives with minimal impact on unit availability.

As erosion and corrosion continue to take their toll, we expect major replacement problems in the areas of piping, pumps and ductwork. How successfully we can sustain a meaningful level of production from these units 5 or 10 years from now remains to be seen.

## Session 3: DUAL ALKALI

Norman Kaplan, Chairman
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

# RESULTS OF THE DOWA TECHNOLOGY TESTS AT THE SHAWNEE SCRUBBER FACILITY

By

G. Hollinden, R. Runyan, S. Newton, F. Garrison
Division of Energy Demonstration and Technology
Office of Power
Tennessee Valley Authority

S. Pfeffer, D. Smith
Air Correction Division
UOP Inc.

## ABSTRACT

The Dowa process for $SO_2$ removal combines the benefits of solution scrubbing, the use of limestone, and the production of stable gypsum as the waste product. This report will discuss the results of the test program performed at the TVA test facility from January through April, 1982.

The objective of the test program was to demonstrate the operation of the Dowa process for sulfur dioxide removal from flue gas generated by a coal-fired boiler.

A test program was conducted at Shawnee during 1979-1980 which demonstrated $SO_2$ absorption and regeneration of the scrubbing liquor, but there was insufficient time for long term reliability tests and there was no provision for the aluminum regeneration subsystem during this program. The current program was conducted after significant modifications and additions were made to the original system to improve operability and reliability and to insure that the program objectives would be met.

The system has demonstrated the following performance:

- Reliable, scale-free operation
- 80% to 95% $SO_2$ removal depending upon operating conditions (see data pages 8 and 9)
- 100% utilization of limestone (1.0 stoichiometry--one mole limestone per mole of $SO_2$ removed)
- 80+% gypsum solids in filter cake
- 0.06 weight percent or less aluminum in the filter cake
- Efficient mist eliminator operation with minimal wash requirements

Typical startup problems affected initial reliability of the system. The nature of the problems experienced and their solutions are discussed.

## LEGAL NOTICE

This publication was prepared by the Tennessee Valley Authority (TVA) and the Air Correction Division of UOP Inc. as an account of work sponsored by the United States Department of Energy (DOE), TVA, and UOP. Neither DOE, members of DOE, TVA, nor UOP, or any person acting on behalf of either: (a) makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or (b) assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this publication. This paper does not necessarily reflect the views and policies of the TVA.

# INTRODUCTION

The Dowa process is a dual-alkali flue gas desulfurization (FGD) process which utilizes basic aluminum sulfate solution for $SO_2$ absorption and limestone for regeneration of the absorbent. The process was developed by the Dowa Mining Company of Tokyo, Japan, and is marketed in the United States under an exclusive license arrangement by the Air Correction Division of UOP Inc. The process is now in commercial operation in Japan at an oil-fired boiler, smelters, and sulfuric acid plants. The Shawnee prototype Dowa installation is treating flue gas from a coal-fired boiler.

Potential advantages of the Dowa process over the conventional limestone scrubbing process which were justification for the Shawnee tests are:

- Utilizes solution scrubbing versus slurry scrubbing to eliminate erosion of equipment and slurry solids buildup on mist eliminator and absorber internals.
- Requires lower limestone stoichiometry.
- Produces a gypsum byproduct which has better dewatering characteristics than unoxidized limestone scrubbing sludge. The Dowa gypsum made in Japan is used for wallboard production.

During 1979-1980, a six-month Dowa test program at Shawnee was funded by EPRI, TVA, and UOP. The results from that work indicated that additional testing was recommended.

The current Dowa technology tests at Shawnee were jointly funded by the United States Department of Energy (DOE), the Tennessee Valley Authority (TVA), and UOP Inc. The objective of this test program was to demonstrate totally integrated operation of the Dowa process for sulfur dioxide removal from flue gas generated by a coal-fired utility boiler. Specifically:

- To demonstrate the $SO_2$ removal efficiency and reliability of the Dowa process over a range of operating conditions simulating typical power plant operation.
- To verify design parameters for scale-up to a full-scale FGD system.
- To evaluate the physical properties of the gypsum byproduct.
- To demonstrate the performance of the aluminum regeneration system.
- To simulate performance of the Dowa process at design flue gas flow rates of specific interest to TVA.

Shawnee Train 200, a limestone scrubber system, was modified to the Dowa configuration and a four-month test program was conducted. This program consisted of one month of start-up/shakedown related activities followed by three months of testing at various flue gas flow rates.

## PROCESS CHEMISTRY

The overall chemical reactions in each of the major process steps are:

- Absorption:

$$Al_2(SO_4)_3 \cdot Al_20_3 + 3SO_2 \longrightarrow Al_2(SO_4)_3 \cdot Al_2(SO_3)_3 \tag{1}$$

- Oxidation:

$$Al_2(SO_4)_3 \cdot Al_2(SO_3)_3 + 3/20_2 \longrightarrow Al_2(SO_4)_3 \cdot Al_2(SO_4)_3 \tag{2}$$

- Neutralization:

$$Al_2(SO_4)_3 \cdot Al_2(SO_4)_3 + 3CaCO_3 + 6H_20 \longrightarrow Al_2(SO_4)_3 \cdot Al_20_3 + 3(CaSO_4 \cdot 2H_20) + 3CO_2 \tag{3}$$

- Aluminum Recovery:

$$Al_2(SO_4)_3 + 3CaCO_3 + 9H_2O \longrightarrow 2Al(OH)_3 + 3(CaSO_4 \cdot 2H_20) + 3CO_2$$

The process is more accurately defined by the principal intermediate steps within the four overall process steps, as follows:

- Absorption

$$SO_2(g) \longrightarrow SO_2\ (diss.) \tag{4}$$

$$SO_2(diss.) \rightleftharpoons H_2SO_3(diss.) \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons H^+ + SO_3^{-2} \tag{5}$$

The last step in the dissociation does not proceed at pH3.

- Oxidation

$$HSO_3^- + 1/20_2 \longrightarrow H^+ + SO_4^{-2} \tag{6}$$

- Neutralization

$$SO_4^{-2} + CaCO_3(s) + 2H_20 \longrightarrow CaSO_4 \cdot 2H_20(s) \quad + CO_3^{-2} \tag{7}$$

$$CO_3^{-2} + H_20 \rightleftharpoons HCO_3^- + OH^- \tag{8}$$

$$HCO_3^- + H_20 \rightleftharpoons H_2CO_3 + OH^- \tag{9}$$

$$H_2CO_3(diss.) \rightleftharpoons H_20 + CO_2(diss.) \rightleftharpoons CO_2(g) \tag{10}$$

The last reaction goes to completion at pH3.

Control of the process chemistry requires measurement and control of the total aluminum concentration in the process liquor and the percentage of this aluminum available for the $SO_2$ absorption reactions. The aluminum concentration is monitored by routine laboratory analysis and controlled by addition of aluminum sulfate solution to the absorber hold tank. The percentage of the aluminum available for absorption is controlled by measurement and control of "% basicity." The concept of % basicity is defined in the following discussion.

Within the composition range of interest, the liquor pH only changes by 0.2 to 0.5 pH units, typically between 3.0 and 3.5. This small pH change precludes the use of pH as a process control mechanism. Therefore, in the Dowa process, process control is based upon liquor composition using basicity, B, which is defined as follows:

$$B\ (\%) = \frac{1}{3} \frac{M_{OH}}{M_{Al}} 100$$

Where $\frac{M_{OH}}{M_{Al}}$ = the ratio of moles of hydroxide ion per mole of aluminum ion present

As examples of the concept of basicity, consider the following:

| Compound | Basicity<br>% |
|---|---|
| $Al_2(SO_4)_3$ | 0 |
| $Al(OH)_x^{+(3-x)}$ | $\frac{100x}{3}$ |
| $Al(OH)_3$ | 100 |

Three independent means of determining liquor basicity can be used. The liquor basicity is monitored by an on-line basicity analyzer which determines the liquor basicity on a continuous basis. In addition, the liquor basicity can be determined by direct titration in the laboratory or calculated from the results of an analysis of a liquor sample. The on-line basicity monitor was the only method used for process control during the Shawnee tests.

## SHAWNEE DOWA PROCESS EQUIPMENT DESCRIPTION

Figure 1 is a flow diagram of the Shawnee Train 200 after modifications required to convert the original limestone system to the Dowa process. Major process equipment utilized included:

1) The existing scrubber (the nitrile foam spheres were replaced with packing and a new mist eliminator was added).

2) An existing air compressor was used to inject air into the new Dowa oxidation nozzle and oxidation tower.

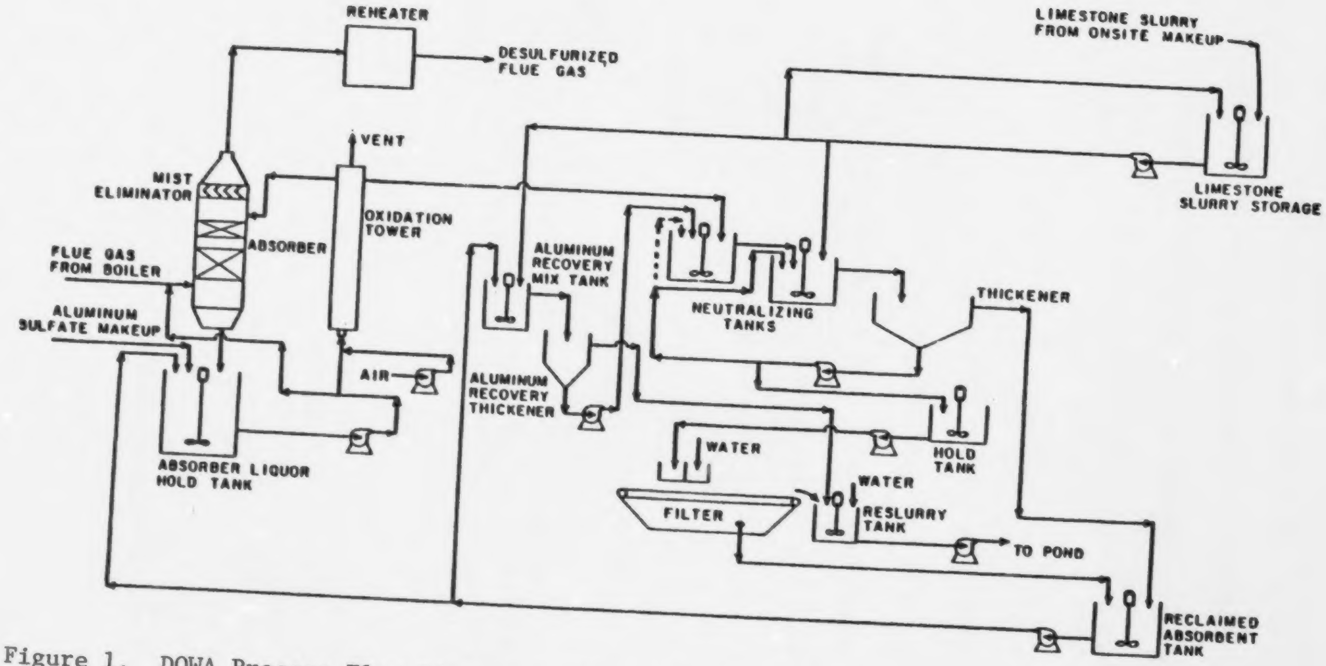


Figure 1. DOWA Process Flow Diagram - Shawnee Test Facility

3) Two neutralization tanks, one for limestone neutralization of the aluminum sulfate solution, the second for redissolution of the precipitated aluminum hydroxide from the aluminum recovery subsystem.

4) An existing thickener used for initial gypsum dewatering.

5) An existing horizontal-belt vacuum filter for final gypsum dewatering.

6) An aluminum recovery system consisting of a mix tank followed by a coned bottom settler.

7) A reclaimed absorbent hold tank.

8) An aluminum sulfate solution feed system.

9) All process pumps and agitators associated with the above equipment.

Sulfur dioxide absorption occurs in the packed absorber where Dowa scrubbing solution is counter-currently contacted with the incoming flue gas. The oxidation of sulfite occurs in the absorber and in the oxidation tower. A bleedstream of absorbent is pumped to the neutralizer tank, where limestone required for neutralization is added. The neutralizer product overflows into a conventional thickener. The thickener overflow is collected in the reclaimed absorbent tank. The thickener underflow is pumped to a surge tank prior to final dewatering of the gypsum byproduct by the belt filter. A portion of the thickener underflow is recycled to the neutralization tank to provide gypsum seed crystals for the neutralization/gypsum precipitation step.

The basicity of the absorbent in the absorber loop and the reclaimed absorbent is continuously monitored with an on-line basicity analyzer and routinely analyzed in the test facility laboratory. The basicity of the reclaimed absorbent is controlled by varying the limestone feedrate to the neutralization tank. The basicity of the liquor in the absorber loop is controlled by varying the rate of the absorbent purge to the neutralization section.

The aluminum concentration in the absorbent is monitored by laboratory analysis and controlled by aluminum sulfate solution addition. The level of soluble impurities in the absorbent is controlled by overflowing a slipstream of thickener overflow to the aluminum recovery system. An excess of limestone is added in a mix tank to precipitate the aluminum as aluminum hydroxide. The mix tank overflows into a coned bottom clarifier where the aluminum hydroxide and excess limestone are separated from the solution. The aluminum recovery settler underflow is redissolved in the absorber bleedstream to reclaim the aluminum content and excess limestone. The soluble impurities present in the overflow are purged from the system.

## TEST RESULTS

The test conditions selected for the Dowa demonstration were geared to reflect typical operating conditions expected in a full scale commercial Dowa system. The range of variables and design points for the test work is as follows:

| | |
|---|---|
| Flue gas flow rate, acfm at 300°F | 16,500 - 27,500 |
| Absorber superficial gas velocity, fps | 7.5 - 12.5 |
| Inlet $SO_2$ concentration, ppm | 1,500 - 2,500 (uncontrolled) |
| Inlet particulate concentration, gr/dscf | 0.4 - 0.8 |
| Oxidation air rate, scfm | 120 - 140 |
| Liquor rate to absorber, gpm | 600 - 830 |
| Absorber packing height, ft. | 10 (6' + 4') |
| Nominal aluminum concentration, g/L | 20 |
| Absorber liquor basicity, % | 10 |
| Regenerated liquor basicity, % | 30 |
| Redissolution tank basicity, % | 15 |
| Solids concentration in neutralization tank, wt. % | 10 |
| Thickener underflow solids concentration, wt. % | 35 |
| Feed to aluminum recovery system, gpm | 1.5 - 2.9 |

The absorber was initially configured with 10 feet of packing. The following table summarizes the results obtained using this packing configuration.

| | TEST NUMBER | |
|---|---|---|
| | DSD-1 | DSD-2 |
| Absorber gas rate, acfm @ 250°F | 16,500 | 19,100 |
| Absorber superficial gas velocity, fps | 7.5 | 8.7 |
| Liquid rate, gpm to absorber packing | 635 | 620 |
| L/G, gal/kcf saturated | 45 | 38 |
| Limestone stoichiometry<br>(1 mole Ca/mole $SO_2$ removed) | 1.0 | 1.0 |
| $SO_2$ removal % | 95 | 96 |
| Absorber $\Delta P$, inches w.c. | 8.2 | 11.6 |

As can be seen from the above table, the $SO_2$ removal was very good using this packing but the absorber pressure drop was higher than what was predicted by the packing manufacturer. Due to the high pressure drop and TVA's interest in testing the Dowa system at higher gas velocities, a decision was made to replace this packing with a packing containing less surface area per cubic foot of fill. The following tests were completed using 10 feet of this new packing.

| | TEST NUMBER | | | |
|---|---|---|---|---|
| | DSD-3 | DSD-4 | DSD-5 | DSD-6 |
| Absorber gas rate, acfm @ 250°F | 19,100 | 19,100 | 27,000 | 16,500 |
| Absorber superficial gas velocity, fps | 8.7 | 8.7 | 12.3 | 7.5 |
| Liquid rate, gpm to absorber packing | 647 | 687 | 761 | 652 |
| L/G, gal/kcf saturated | 40 | 42 | 33 | 46 |
| Limestone stoichiometry (1 mole Ca/mole $SO_2$ removed) | 1.0 | 1.0 | 1.0 | 1.0 |
| $SO_2$ removal, % | 82 | 84 | 82 | 92 |
| Absorber $\Delta$P, inches w.c. | 2.2 | 2.3 | 8.1 | 1.7 |

The above results achieved the desired low absorber pressure drops, however, the $SO_2$ removal fell below the 90% level at the higher gas velocities. In order to demonstrate high $SO_2$ removal efficiency and low pressure drop a combination of the two styles of packing was installed. This configuration consisted of 6 feet of packing as used in tests DSD-3 through 6 followed by 4 feet of packing similar to that used in tests DSD-1 and 2 . The results obtained with this configuration are as follows:

| | TEST NUMBER | | | | | |
|---|---|---|---|---|---|---|
| | DSD-7 | DSD-8 | DSD-9 | DSD-10 | DSD-11* | DSD-12 |
| Absorber gas rate, acfm @ 250°F | 23,800 | 24,500 | 19,100 | 19,100 | 26,000 | 16,500 |
| Absorber superficial gas velocity, fps | 10.8 | 11.1 | 8.7 | 8.7 | 12.5 | 7.5 |
| Liquor rate, gpm to absorber packing | 640 | 750 | 640 | 690 | 740 | 640 |
| L/G, gal/kcf saturated | 31 | 36 | 39 | 42 | | 45 |
| Limestone Stoichiometry | 1.0 | 1.0 | 1.0 | 1.0 | | 1.0 |
| $SO_2$ removal, % | 83 | 87 | 92 | 94 | | 95 |
| Absorber $\Delta$P, inches w.c. | 5.0 | 8.8 | 2.5 | 2.7 | | 2.0 |

* Attempts were made to run at 12.5 fps absorber superficial gas velocity with this packing but flooding conditions were encountered.

### Gypsum Quality

Throughout much of the testing, problems were encountered with the operation of the gypsum horizontal-belt filter. These problems included process and mechanical related upsets. During the test program, changes were made to the existing belt filter aimed at improving the quality of the gypsum end product. The original filter cloth was replaced with a more porous cloth material and the belt width was reduced from four feet to one foot. The washing scheme was modified to allow one stage of filtrate wash followed by one stage of fresh water wash. These modifications resulted in an improved gypsum quality but the gypsum now dewatered too rapidly, not allowing a level of filter feed or wash water to be retained above the filter cake. Despite this fact, gypsum of good quality was produced. Typical composition of the gypsum produced is listed below:

| Component | % by Wt. (dry) |
|---|---|
| Al | 0.06 |
| Ca | 27 |
| $CO_3$ | <0.1 |
| $SO_3$ | 0 |
| $SO_4$ | 70 |
| Total Solids | 80-85 |
| Acid Insolubles (flyash) | 2-5 |

## OPERABILITY AND RELIABILITY

Completion of the modifications necessary to convert the existing Train 200 limestone system to the Dowa process occurred in late December, 1981. Following the completion of construction, equipment-related start-up problems prevented continuous, stable operating conditions until February, 1982. These start-up related problems included corrosion of carbon steel components that were inadvertently left in the Dowa system after its conversion.

During this startup phase, intermittent excursions in sulfite levels were noted. Samples containing the unoxidized sulfites were sent to UOP's Corporate laboratories in Des Plaines. It was observed that oil was getting into the Dowa process from the exit gas reheater as well as lubricating oil from the belt filter. Tests conducted by UOP showed that oils, when emulsified with the Dowa solution as would occur in the oxidation tower, reduced the rate of oxygen transfer from the gas phase into the liquid. The presence of unoxidized sulfites in the solution suppress $SO_2$ removal due to a higher vapor pressure of $SO_2$ over the solution. During periods of operation when oils were found to be present, an increase of 15% oxidation air rate and liquid recycle rate overcame the problem and allowed 100% sulfite oxidation. Modified procedures for lighting the reheater and minimizing introduction of oil into the system have been undertaken. No further sulfite oxidation problems have occurred.

After the startup and initial operating phase of the program the system performed with a high degree of reliability. The following table represents the availability of the system from February through April. Availability is defined as:

$$\text{Availability} = \frac{\text{hours Dowa system operated}}{\text{period hours - outage hours not caused by Dowa process}}$$

| WEEK | AVAILABILITY<br>% | REASON FOR SYSTEM BEING DOWN |
|---|---|---|
| 2/1 | 100.0 | |
| 2/8 | 100.0 | |
| 2/15 | 100.0 | |
| 2/22 | 100.0 | |
| 3/1 | 100.0 | |
| 3/8 | 81.8 | Repair G-201 recycle pump |
| 3/15 | 100.0 | |
| 3/22 | 93.2 | Repair G-201 recycle pump seal water leak |
| 3/29 | 100.0 | |
| 4/5 | 98.1 | Repair G-201 recycle pump bearing |
| 4/12 | 75.8 | Finish repairs on G-201 pump bearing |
| 4/19 | 100.0 | |
| Overall Availability | 95.7 | |

The primary cause of downtime resulted from pump bearing and seal problems. It should be noted that if in-line spare pumps were installed as in a commercial system, these outages would not have affected availability. The scheduled downtime to change out the packing and outages caused by reheater and ID fan problems has not been included in calculating availability.

The demonstration was performed utilizing flue gas taken downstream of a small, retired electrostratic precipitator that was reactivated for this program. This resulted in fly ash loadings entering the Dowa scrubber of between 0.4 and 0.8 grains/dscf. Typically, the Dowa scrubbing liquor contained 1.5 to 2.0% suspended fly ash solids. There was no notice of any detrimental process related problems as a result of these high fly ash loadings. The fly ash removed by the system ultimately ends up in the byproduct gypsum cake. Upon inspection of the packing and mist eliminator there were no indications of any detrimental solid deposits or buildup.

Throughout the test program, the mist eliminator performed well. The mist eliminator was washed for three minutes, once per day, at a rate of 12 gpm. Even with this infrequent washing and suspended fly ash in the scrubbing liquor, the mist eliminator remained free of solids buildup.

## CONCLUSIONS AND RECOMMENDATIONS

Based on the results obtained during this recent test work at the Shawnee scrubber facility:

- The Dowa process has demonstrated its ability to reliably remove $SO_2$ from coal derived flue gas over a range of operating conditions simulating typical power plant operation (see pages 8 and 9).
- Design parameters to be used in designing a full-scale Dowa FGD system have been verified.
- The physical properties of the byproduct gypsum have been investigated. UOP is performing further laboratory test work to optimize the use of filtrate and fresh water to further improve the quality of the gypsum cake.
- The performance of the aluminum regeneration system has demonstrated its ability to control the concentration of soluble impurities within a range acceptable to the Dowa process.
- Ninety percent $SO_2$ removal was not demonstrated at 12.5 ft/sec absorber velocity.
- The Dowa process reliably treated flue gas containing high (0.4-0.8 gr/dscf) fly ash loadings without detrimental effects on the process.
- UOP feels the test results from this program, coupled with the process reliability demonstrated throughout this work, reinforces their confidence in offering the Dowa process on a commercial full-scale basis.

# FULL-SCALE DUAL ALKALI FGD DEMONSTRATION AT LOUISVILLE GAS AND ELECTRIC COMPANY

by: Norman Kaplan
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Elizabeth D. Gibson and Lawrence R. Woodland
Arthur D. Little, Inc.
20 Acorn Park
Cambridge, MA 02140

## ABSTRACT

This paper summarizes results from the recently completed full-scale demonstration program of the dual alkali FGD system at Louisville Gas and Electric Company's (LG&E's) Cane Run Unit 6. The demonstration program included a 12-day acceptance test, an official demonstration period of 13 months, and 4 additional months of system monitoring and instrument calibration.

The FGD system designer offered LG&E seven process performance guarantees applying to: $SO_2$ emissions, particulate matter emissions, lime consumption, soda ash consumption, power consumption, waste solids properties, and system availability. All performance guarantees were met during the demonstration program except waste solids properties and soda ash consumption. These two guarantees were not met primarily because of problems related to operation of the vacuum filters. (However, the soda ash consumption guarantee was met during the 12-day acceptance test.) $SO_2$ removal averaged 91.6% during both the 13-month demonstration period and the 12-day acceptance test.

Monthly performance parameters were applied throughout the 13-month demonstration period to characterize system operation. FGD system availability and utilization were 93.23% and 77.42%, respectively; system reliability was 94.06%, and operability was 94.01%.

## NOTES

1. Company Names and Products

   The mention of company names or products is not to be considered an endorsement or recommendation for use by the U.S. Environmental Protection Agency.

2. Units of Measure

   EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice will result in undue cost or difficulty in clarity, IERL-RTP provides conversion factors for the non-metric units. Generally, this paper uses British units of measure.

   The following equivalents can be used for conversion to the metric system:

| British | Metric |
|---|---|
| Btu | 1055 J |
| 5/9 (°F-32) | °C |
| 1 ft | 0.3048 m |
| 1 ft$^3$ | 0.0283 m$^3$ |
| 1 in. | 2.54 cm |
| 1 lb (avoir.) | 0.4536 kg |
| 1 ton (long) | 1.0160 m tons |
| 1 gal | 3.7854 liters |
| lb/10$^6$ Btu | 430 ng/J |
| ft/hr | .508 cm/min |

# 1.0 INTRODUCTION

The purpose of this program was to demonstrate the full-scale utility application of dual alkali flue gas desulfurization (FGD) technology. The program was a joint effort by several organizations under the sponsorship of the Environmental Protection Agency (EPA). The system was designed by the air pollution control group of Combustion Equipment Associates (CEA, now part of Thyssen-CEA Environmental Systems, Inc.) and Arthur D. Little, Inc. (ADL) and installed on Unit 6 of Louisville Gas and Electric Company's Cane Run Station in Louisville, Kentucky, an existing 300-MW (gross peak capacity) coal-fired boiler burning high sulfur coal.

The FGD system was installed to comply with the requirements of the Jefferson County Air Pollution Control District, the Kentucky State Division of Air Pollution, and Region 4 of the U.S. EPA (85% removal of $SO_2$). Installation was by the construction department of LG&E, with technical guidance on process design from CEA.

The two major goals of the demonstration were to establish:

- Overall performance -- $SO_2$ removal, lime consumption, soda ash consumption, regeneration of spent liquor, water balance, evaluation of scaling or solids buildup, evaluation of materials of construction, waste cake properties, and system dependability.

- Economics -- capital investment and operating cost.

The scope of work for the overall program included the design, construction, start-up, acceptance testing, and 1-year operation of a CEA/ADL concentrated-mode dual alkali FGD system. The program was divided into four phases:

- Phase I -- preliminary design and cost estimates.

- Phase II -- engineering, design, construction, and mechanical testing.

- Phase III -- start-up and acceptance testing.

- Phase IV -- 1 year of operation and demonstration testing.

LG&E was the prime contractor with overall responsibility for constructing and operating the system. CEA, under subcontract to LG&E, was responsible for the engineering design, for supplying all process equipment, and for providing engineering assistance during start-up and acceptance testing. CEA was also responsible for compliance with all process guarantees and equipment warrantees. ADL, under subcontract to CEA, supplied process engineering support to CEA during design, start-up, and acceptance testing; and gave process assistance to LG&E for system operation during the 13-month demonstration period. ADL is also responsible for preparing all reports required under the EPA/LG&E contract.

Bechtel National, Inc., under separate contract with EPA, conducted an independent test program to assess system performance with respect to the guarantees offered by LG&E and CEA/ADL and to monitor and characterize system performance throughout the demonstration program.

Construction was completed in March 1979, and the system was initially charged and started up in April 1979. Various problems with the boiler, the FGD system, and the quality and quantity of lime supplied to the system delayed the acceptance testing until after the demonstration period had begun. The acceptance test was successfully conducted in July 1980, when Unit 6 and all FGD system components were fully and simultaneously available, and the boiler could be operated at (or near) full load (1). The demonstration period officially started on May 1, 1980, and ended on May 31, 1981. System monitoring and instrument calibration continued until September 11, 1981, when the boiler was taken off-line for turbine overhaul.

## 2.0 DESCRIPTION OF THE DUAL ALKALI SYSTEM AT LG&E

Dual (or double) alkali is a generic term applied to FGD systems that use soluble alkali to absorb $SO_2$ and then react the spent scrubber solution with lime and/or limestone to regenerate the alkali and produce a waste calcium-sulfur salt for disposal.

The dual alkali FGD process was developed to overcome the disadvantages of lime and limestone scrubbing (such as scaling) while retaining the cost advantages of a throwaway system. The two principal features of dual alkali technology that distinguish it from conventional direct lime and limestone scrubbing are: (1) the use of a clear solution rather than a slurry for contacting the flue gas in the absorber; and (2) reaction of the solution in a separate absorbent regeneration section to form the waste solids rather than forming the waste solids as a part of the scrubbing operation. Using a scrubbing solution instead of a slurry minimizes scale potential in the scrubber circuit and enables high $SO_2$ removal efficiencies to be achieved over a wide range of inlet $SO_2$ concentrations. Precipitation of the waste calcium sulfite/sulfate solids outside the scrubber facilitates formation of waste solids with good dewatering properties.

Figure 1 is a process flow schematic of the dual alkali system at Cane Run Unit 6. Flue gas from the boiler passes through the electrostatic precipitators and is fed to two absorbers. A recyling sodium sulfite solution, flowing countercurrent to the flue gas across two stainless steel perforated plate trays, absorbs $SO_2$ according to the following reaction:

$$SO_3^{=} + SO_2 + H_2O \rightarrow 2HSO_3^{-}$$

In addition, due to oxidation of sulfite ion in solution, sulfate ($SO_4^{=}$) is formed in the absorbent liquor:

$$SO_3^{=} + 1/2\ O_2 \rightarrow SO_4^{=}$$

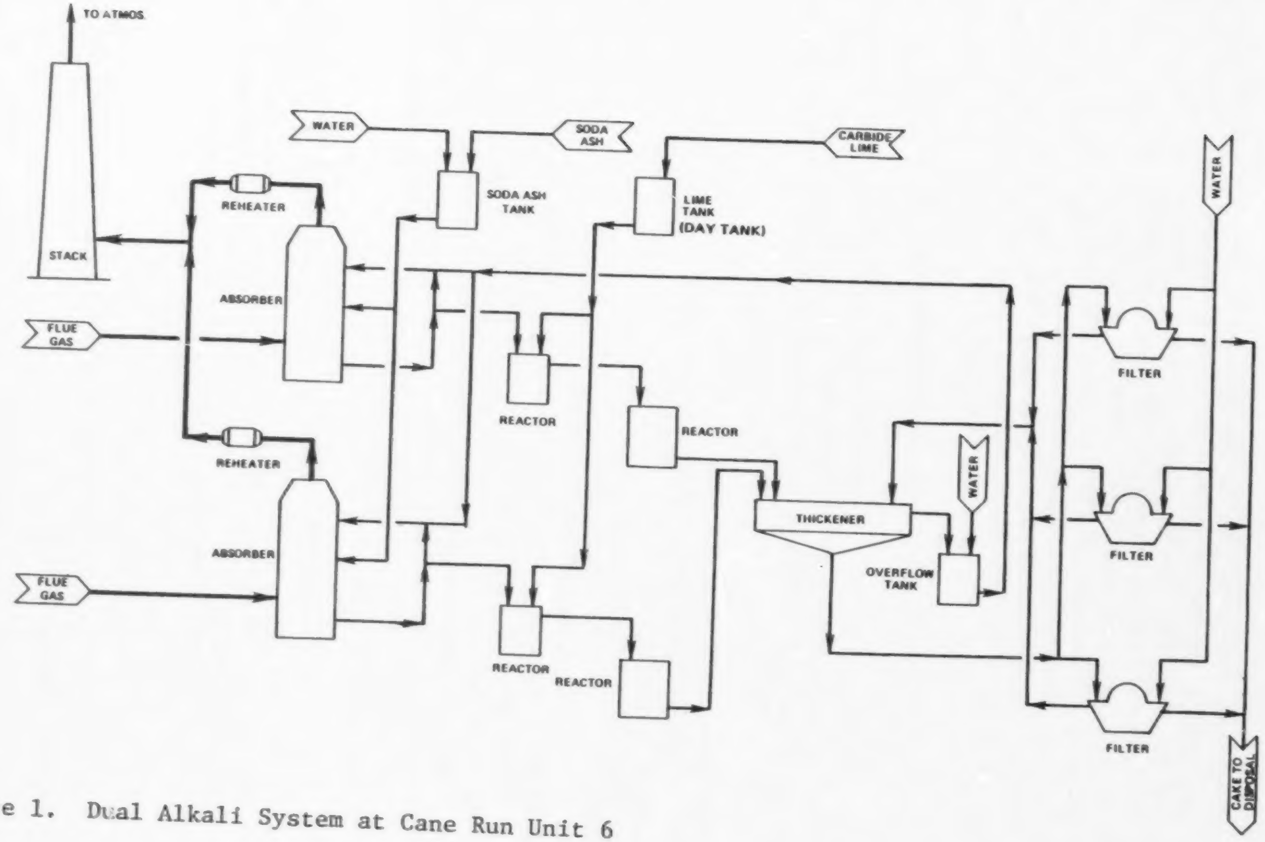


Figure 1. Dual Alkali System at Cane Run Unit 6

The scrubbed flue gas is reheated by combustion gases from a direct-fired oil reheater and is ducted to the stack.

Sodium carbonate is added to either the thickener or the absorber to make up for normal losses of sodium in the system. Bleed streams of the spent absorbent solution from the absorbers are sent to the regeneration reactor trains where carbide lime is added to convert the bisulfite ($HSO_3^-$) in the spent absorbent to sulfite ($SO_3^=$) in the regenerated absorbent, precipitating a mixture of calcium sulfite and sulfate solids:

$$2HSO_3^- + Ca(OH)_2 \rightarrow CaSO_3\downarrow + SO_3^= + 2H_2O$$

$$SO_4^= + 2HSO_3^- + Ca(OH)_2 \rightarrow CaSO_4\downarrow + 2H_2O + 2SO_3^=$$

The mixed solids actually can be designated as: $xCaSO_3 \quad yCaSO_4 \quad z\ H_2O$; where the ratio x:y is usually greater than 4, and z represents some amount of water of hydration. No pure gypsum phase is formed. The solids are separated from the liquor in a thickener and are removed from the system on washed rotary vacuum filters. The clear liquor overflowing from the thickener is returned to the absorber recycle loop. The filter cake is mixed with fly ash and quicklime via the Conversion Systems, Inc. (CSI) process. After fixation the solids are trucked to a landfill site for disposal.

Table 1 compares the design basis with the observed operation of the system. The LG&E installation was designed to operate with a liquid-to-gas (L/G) ratio of less than 10 gal./$10^3$ acf, including liquor feed to the tray and spray recycle. (Typical lime/limestone slurry processes are designed for an L/G of about 50 to 100 gal./$10^3$ acf.)

## 3.0 PROCESS GUARANTEES AND SYSTEM PERFORMANCE

The CEA/ADL dual alkali system was designed to meet seven process performance guarantees applying to: $SO_2$ emissions, particulate matter emissions, lime consumption, soda ash consumption, power consumption, waste solids properties, and system availability. These guarantees were offered LG&E by CEA/ADL and passed through in the contract between EPA and LG&E. A 12-day acceptance test, conducted from July 17 to July 28, 1980, measured the performance of the dual alkali system in terms of the guarantees. $SO_2$ emissions were continuously measured. Filter cake samples were analyzed periodically to determine lime and soda ash consumption and the insoluble solids content of the filter cake. Power consumption was directly monitored. The process guarantees were also used throughout the 13-month demonstration period to monitor system performance on a long-term basis.

### 3.1 ACCEPTANCE TEST RESULTS

Table 2 summarizes the performance guarantees and the corresponding results of the acceptance test. As shown, the FGD system did meet all performance guarantees during the acceptance test, with the exception of the filter cake properties.

## TABLE 1. FGD SYSTEM PERFORMANCE CONDITIONS

| | Design | Observed[a] |
|---|---|---|
| **Coal (Dry Basis)** | | |
| Sulfur | 5.0% S | 3.5% S |
| Chloride | 0.04% Cl | 0.02% Cl |
| Heat Content | 11,000 Btu/lb | 10,650 Btu/lb |
| **Inlet Gas** | | |
| Flow Rate (Volumetric) | 1,065,000 acfm | 1,045,000 acfm |
| Temperature | 300°F | 280°F |
| $SO_2$ | 3471 ppm | 2180 ppm |
| $O_2$ | 5.9% | 7.7% |
| Particulate Matter | 0.10 lb/$10^6$ Btu | 0.84 lb/$10^6$ Btu |
| **Outlet Gas** | | |
| $SO_2$ | $\leq$200 ppm | 183 ppm |
| Particulate Matter | 0.10 lb/$10^6$ Btu | 0.10 lb/$10^6$ Btu |
| **Boiler** | | |
| Generation (Net) | 280 MW | 250 MW |

[a] All figures shown represent average values, except for inlet gas flow rate, temperature, and boiler generation, which are maximum values.

TABLE 2. PERFORMANCE GUARANTEES AND ACCEPTANCE TEST RESULTS

| Guarantee | Test Results |
|---|---|
| **$SO_2$ Emissions** | |
| 200 ppm (dry basis) without additional air dilution | 143 ppm (dry basis) without additional air dilution |
| **Calcium Consumption** | |
| 1.05 moles available CaO per mole $SO_2$ removed | 1.04 moles available CaO per mole $SO_2$ removed |
| **Soda Ash Consumption** | |
| 0.045 moles $Na_2CO_3$ per mole $SO_2$ removed | 0.042 moles $Na_2CO_3$ per mole $SO_2$ removed |
| **Net Particulate Matter Addition** | |
| No net particulate matter addition by FGD system | Net particulate matter removal efficiency averaged 88% |
| **Power Consumption** | |
| System will consume (excluding reheat) not more than 1.2% of gross peak boiler capacity (300 MW) | System consumed 1.05% of power generated at highest actual boiler operating load (240 MW) |
| **Filter Cake Properties** | |
| Filter cake will contain a minimum of 55 wt % insoluble solids | Filter cake averaged 52.2 wt % insoluble solids |

The acceptance test began at midnight on July 17, 1980. The program ran smoothly for the first 6 days except for the discrepancy in $SO_2$ emission results between the Lear Siegler readings and the EPA Method 6 analysis. This discrepancy was traced to a burned out ground wire in the Lear Siegler system, which resulted in recorded $SO_2$ emission values that were consistently lower than those noted by EPA Method 6 analysis. Based on readings obtained after repair of the ground wire, the Lear Siegler results for the first 6 days were corrected by adding 30 ppm to the hourly and daily averages.

Peak generation during the acceptance test was 240 MW, and the average load was 178 MW. For each test day, the boiler load was raised to its maximum achievable level (240-250 MW) sometime between 0600 and 0800 hours. The load was limited to this level because the FGD system booster fan could handle no more gas volume. Since the boiler was operated with an absorber inlet oxygen concentration of 7.7% (instead of the design of 5.9%), a larger volume of gas was produced at the corresponding generation rate. The system was operating at maximum design gas flowrate (about 1,000,000 acfm), yet only at 80% of design generating capacity. High load was held daily for 10 hours (an acceptance test prerequisite) and then reduced in steps to a low level of about 80 MW for 6-7 hours, generally between midnight and 0700 hours, in line with electrical energy demand.

The test proceeded smoothly until July 23 when wet coal, resulting from heavy rains during the previous night, blocked the coal feeders to the mills. The boiler load was restricted to 150-160 MW for two days. Process stream analysis and stack sampling continued because the FGD system was performing well, but the test program was extended by 2 days to record 10 days of operation at full capacity. By July 25 the wet coal problems subsided, and the program continued to completion at midnight on July 28.

## 3.2 DEMONSTRATION PERIOD RESULTS

Table 3 summarizes system performance in terms of process guarantees over the course of the 13-month demonstration period. Significant variations from the process guarantees are discussed below. As Table 3 shows, the FGD system met all performance guarantees except filter cake insoluble solids and sodium consumption. These two guarantees were not met primarily because of problems related to operation of the vacuum filters. Filter performance depends primarily on the thickness of the filter cake and the amount of cake washing. Manual control of cake thickness requires simultaneous manipulation of filter trough slurry level, drum speed, and thickener underflow solids. It has been possible to obtain the proper filter cake thickness and wash rate under controlled tests and reduce sodium losses to meet the guarantee, but under long-term operation, these filter conditions have not been held.

The power consumption guarantee states that at gross peak boiler load the FGD system will consume a maximum of 1.2% of the power generated by the unit. Many of the power consumption figures and the average shown in Table 3 exceed 1.2%. This is to be expected since power consumption is not a linear function of boiler load, and the figures shown represent periods of operation well below peak load. Table 2 indicates that FGD power consumption was only 1.05% at 240 MW, 80% of gross peak load.

TABLE 3. SUMMARY OF SYSTEM PERFORMANCE IN TERMS OF PROCESS GUARANTEES[a]

|  | $SO_2$ Emissions (ppm)[b] | $SO_2$ Removal (%) | CaO Consumption[c] | $Na_2CO_3$ Consumption[d] | Power Consumption (%) | Insoluble Solids (wt %) | System Availability (%) |
|---|---|---|---|---|---|---|---|
| May 1980 | 130.0 | 93.2 | 1.23 | 0.079 | 1.10 | 55.0 | 99.9 |
| June 1980 | 115.5 | 95.0 | 1.20 | 0.085 | 1.15 | 47.8 | 99.9 |
| July 1980 | 143.0 | 94.4 | 1.04 | 0.042 | 1.05 | 52.2 | 99.9 |
| August 1980 | 131.0 | 93.6 | --[e] | --[e] | -- | --[e] | 99.3 |
| September 1980 | 157.5 | 92.6 | 1.15 | 0.058 | 1.26 | 49.7 | 94.0 |
| October 1980 | 150.0 | 89.8 | 1.04 | 0.076 | 1.43 | 46.8 | 99.9 |
| November 1980 | 312.0 | 82.6 | 0.89 | 0.132 | 1.57 | 36.9 | 85.1 |
| December 1980 | -- | -- | -- | -- | -- | -- | 60.0[f] |
| January 1981 | 205.0 | 91.2 | 1.04 | 0.066 | 1.85 | 49.1 | 84.0 |
| February 1981 | 129.8 | 93.7 | 1.06 | 0.065 | 1.3 | 50.3 | 99.6 |
| March 1981 | 155.7 | 92.0 | 1.04 | 0.069 | 1.7 | 50.5 | 99.8 |
| April 1981 | 143.8 | 93.1 | 0.93 | 0.045 | 1.18 | 52.1 | 98.6 |
| May 1981 | 204.9 | 88.2 | 0.95 | 0.068 | -- | 46.1 | 96.8 |
| Average | 182.9 | 91.6 | 1.05 | 0.071 | 1.36 | 48.8 | 93.2[g] |
| Process Guarantees | 200.0 | -- | 1.05 | 0.045 | 1.20 | 55.0 | 90.0 |

[a] Particulate matter removal efficiency was determined during acceptance test only (88%).

[b] All values shown (except May 1980) are 24-hour average stack $SO_2$ emissions, corrected for moisture and reheater. May 1980 results represent the average of the 2 absorbers' outlet emissions.

[c] Total moles available CaO consumed per mole $SO_2$ removed.

[d] Moles $Na_2CO_3$ consumed per mole $SO_2$ removed.

[e] No filter cake samples were analyzed in August 1980.

[f] FGD system operated only 14.4 hours in December. No system characterization tests were performed.

[g] Average availability based on hours in total period (see Table 4).

During November 1980, the system met the lime consumption guarantee, but did not meet the guarantees for $SO_2$ removal, availability, soda ash consumption, power consumption, and filter cake composition. The poor performance was largely attributed to the presence of significant amounts of suspended solids in the thickener overflow. Extended periods of operation at low boiler load and high oxidation rates caused the ratio of sulfate/sulfite in the scrubbing liquor to become greater than 4:1. At this level of sulfate, the settling characteristics of FGD solids deteriorated, and a significant volume of FGD solids was carried over the thickener weirs and back into what should have been the clear liquor section of the process (hold tank and absorbers). Solids carryover from the thickener overflow increased the rate of absorber plugging and reduced the $SO_2$ removal capability. Lime consumption was extremely low, but this was at the expense of high consumption of soda ash, a more costly material. The high soda ash consumption resulted from reduced washing of the filter cake.

In December 1980, the FGD system operated only for 14 of the 240 hours that No. 6 boiler was in operation, and none of the performance guarantees were met. The boiler was shut down primarily for scheduled maintenenance, and during this outage the FGD system was considered available. However, after the boiler had come back on-line a thickener rake problem rendered the FGD system inoperable for about 300 hours. The rake in the thickener had separated from the drive shaft. The FGD system and the thickener were briefly operated (14 hours) to keep the thickener slurry from freezing and were then shut down so the rake could be repaired. No system characterization tests were performed that month.

## 4.0 MONTHLY PERFORMANCE PARAMETERS AND SYSTEM OPERATION

The operation of the FGD system was monitored monthly on the basis of several performance parameters. These parameters, as defined by the Edison Electric Institute, are shown in Table 4, along with the results for the overall 13-month demonstration period. Table 5 summarizes system performance by month for the official demonstration period (May 1980 through May 1981) and the 4 additional months of monitoring (June through September 1981) covered by this paper.

Major FGD system outages for the period shown in Table 5 were due primarily to difficulties with the thickener and boiler outages. The significant operating problems in December 1980 were caused by excessive solids accumulation in the thickener and separation of the thickener rake from the drive shaft. Thickener problems were again responsible for the FGD system downtime in June 1981, when solids were allowed to accumulate in the thickener because of a false reading indicating low rake torque. Boiler outages accounted for most of the FGD system downtime in September 1981.

Figure 2 shows system availability, operability, and $SO_2$ removal for the 17 months from May 1980 to September 1981.

TABLE 4. AVERAGE PERFORMANCE PARAMETERS[a] FOR DEMONSTRATION PERIOD (APRIL 30, 1980 -- MAY 31, 1981)

| | |
|---|---|
| Period Hours (A) | 9048 |
| Boiler Hours (B) | 7451.5 |
| Percent Boiler Utilization (B/A) | 82.36 |
| FGD Hours (C) | 7005.2 |
| Hours FGD Available (D) | 8435.2 |
| Hours FGD Called Upon (E) | 7447.3 |
| Percent FGD Utilization (C/A) | 77.42 |
| Percent FGD Availability (D/A) | 93.23 |
| Percent FGD Reliability (C/E) | 94.06 |
| Percent FGD Operability (C/B) | 94.01 |

[a] As defined for power plant equipment by the Edison Electric Institute.

# TABLE 5. SUMMARY OF MONTHLY PERFORMANCE PARAMETERS AND $SO_2$ REMOVALS

| | Utilization | Availability | Reliability | Operability | $SO_2$ Removal(%) |
|---|---|---|---|---|---|
| May 1980 | 99.5 | 99.9 | 99.9 | 99.9 | 93.2 |
| June 1980 | 88.9 | 99.9 | 99.9 | 99.7 | 95.0 |
| July 1980 | 83.1 | 99.9 | 99.9 | 99.8 | 94.4 |
| August 1980 | 84.5 | 99.3 | 94.6 | 94.6 | 93.6 |
| September 1980 | 96.9 | 94.0 | 98.8 | 98.6 | 92.6 |
| October 1980 | 99.9 | 99.9 | 99.9 | 99.9 | 89.8 |
| November 1980 | 55.1 | 85.1 | 96.8 | 96.8 | 82.6[a] |
| December 1980 | 1.9 | 60.0 | 6.0 | 6.0 | -- |
| January 1981 | 80.2 | 84.0 | 83.3 | 83.3 | 91.2 |
| February 1981 | 71.6 | 99.6 | 99.5 | 99.5 | 93.7 |
| March 1981 | 71.9 | 99.8 | 99.7 | 99.7 | 92.0 |
| April 1981 | 82.6 | 98.6 | 98.3 | 98.3 | 93.1 |
| May 1981 | 96.8 | 96.8 | 96.8 | 96.8 | 89.8 |
| June 1981 | 26.6 | 71.7 | 48.0 | 48.0 | 90.3 |
| July 1981 | 56.0 | 73.4 | 67.8 | 67.7 | 92.4 |
| August 1981 | 68.3 | 79.7 | 77.1 | 73.3 | 92.9 |
| September 1981 | 22.5 | 99.7 | 98.4 | 98.4 | 92.3 |

[a] FGD system operated only 14.4 hours in December. $SO_2$ removal was not measured.

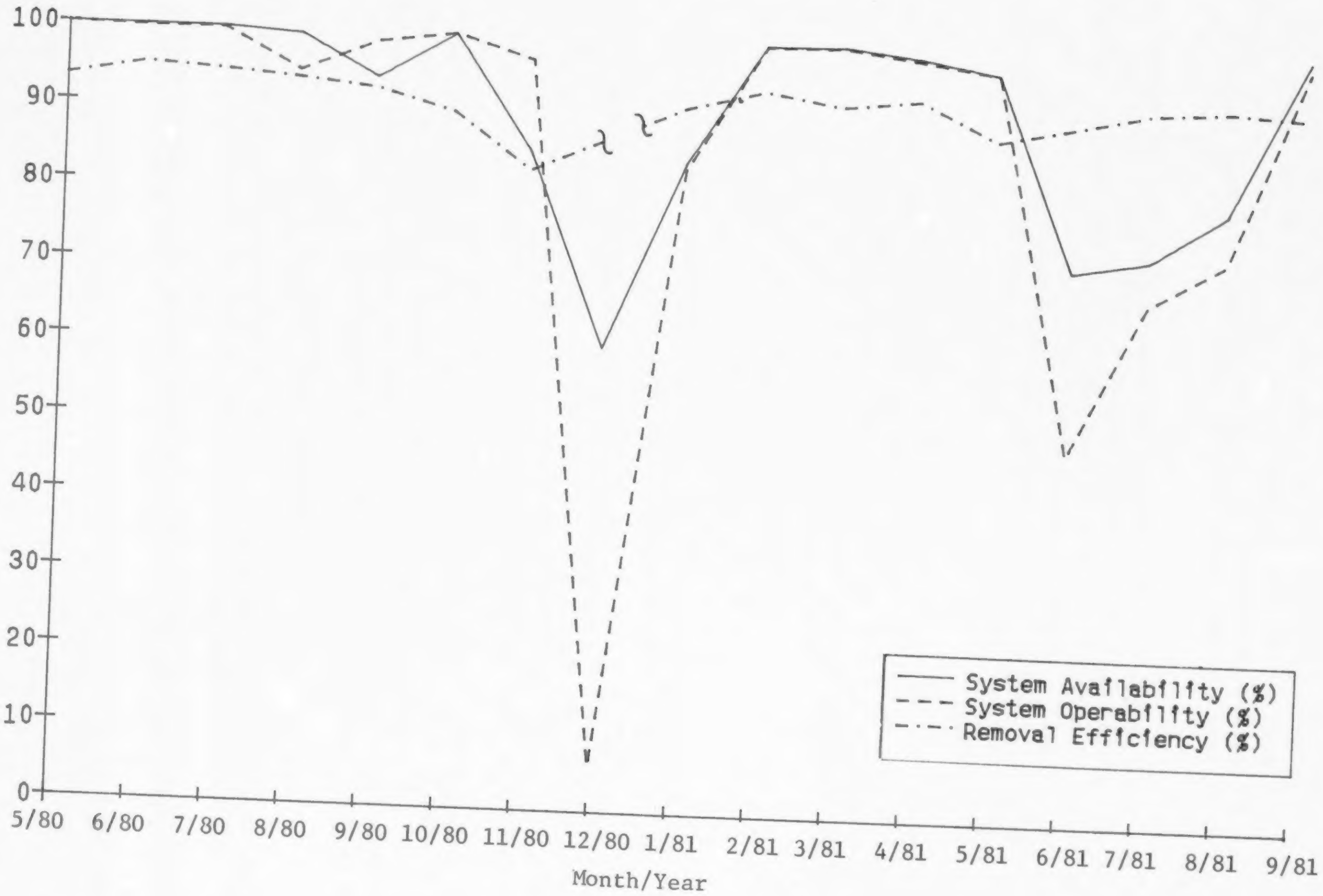


Figure 2. FGD System Availability, Operability, and $SO_2$ Removal Efficiency (May 1980 through September 1981)

## 5.0 CERTIFICATION AND CHECKING OF CONTINUOUS MONITORING INSTRUMENTATION AT LG&E

The primary method of measuring $SO_2$ removal relied on the continuous Lear Siegler monitor (SM-810) installed in the stack and a Dupont 460 analyzer (which alternately sampled the two scrubber inlet gas streams). Inlet flue gas $O_2$ concentrations were monitored by in situ Hagen $O_2$ analyzers, while stack gas $O_2$ concentrations were continuously monitored by a Lear Siegler monitor (CM-50).

After the Lear Siegler stack analyzer had been installed, the system was certified by an outside contractor during December 1979. The system met all the certification requirements called for in the federal regulations (40 CFR 60 Appendix B). Relative accuracy measurements were taken to compare the analyzers' performance with results obtained by EPA reference methods. The measured relative accuracy was 17%, which was within the Federal requirement of less than 20%.

In February 1981 the continuous emission monitoring system was tested by another outside contractor according to the certification procedure specified in 40 CFR 60 Appendix B. The measured relative accuracies for the monitoring instrumentation located at each sampling location were:

- Inlet A -- 17.6%.
- Inlet B -- 14.3%.
- Stack -- 14.9%.

These relative accuracies are within the performance criterion of 20% variation that is specified in 40 CFR 60 Appendix B.

After certification testing, the continuous monitoring instrumentation continued to be checked regularly. To the extent possible, zero and span checks were run daily; relative accuracies and calibration errors were determined every 2 weeks.

EPA Method 6 tests were performed by Bechtel National from June 1981 through September 1981. The tests consisted of several gas analyses of samples from the A inlet, B inlet, and stack. Results were all within the 20% relative accuracy criterion (40 CFR 60 Appendix B) except for one stack sample measured on July 8, 1981 at a value of 21.2% (Table 6).

## 6.0 COMMERCIAL LIME TEST

Airco carbide lime, a by-product of acetylene production, is normally used to regenerate the sodium-based scrubbing liquor at Cane Run. A month-long test with commercial-grade lime in place of carbide lime was conducted as part of the demonstration to compare the performance of the two materials in a lime-based dual alkali system. The specific goals of the commercial-grade lime test were to:

TABLE 6. $SO_2$ RELATIVE ACCURACY MEASUREMENTS[a]

| | Relative Accuracy (%)[b] | | |
|---|---|---|---|
| Test Period | Inlet A | Inlet B | Stack |
| June 1981 | 6.1 | 6.8 | 17.3 |
| July 1981 | 7.4 | 7.0 | 21.2 |
| | 9.6 | 9.9 | 9.4 |
| | 10.8 | 14.7 | 8.3 |
| August 1981 | 5.4 | 5.8 | 6.7 |
| | 7.4 | 11.3 | 8.5 |
| September 1981 | | | 8.5 |

[a] Each relative accuracy value shown represents the average of several test runs and is based on $SO_2$ emissions expressed in $lb/10^6$ Btu for comparison to the 20% performance criterion specified in 40 CFR 60 Appendix B.

[b] Relative Accuracy is defined as:

$$\frac{\text{Absolute Value of Mean Difference + 95\% Confidence Interval}}{\text{Mean of Reference Method}} \times 100$$

- Operate the reactor at a higher pH to allow lower liquor flow rates and longer thickener settling time.

- Increase the rate and control of the regeneration reaction.

- Improve the settling and filtering properties of the waste solids.

The overall conclusion from the commercial-grade lime tests was that the FGD system performance with commercial lime did not differ significantly from its performance with carbide lime. The anticipated improvements in solids settling and filtration were not realized.

## 6.1 EFFECT OF HIGH pH

Because the commercial lime test was to be performed at high reactor pH (>11.0), there was an increased potential for aluminum dissolution (from fly ash carried over to the scrubber) and scaling of the scrubber trays. Aluminum compounds are normally introduced to the system by both the fly ash and carbide lime. At a reactor pH above 10.0, aluminum dissolves in the scrubbing liquor. A scaling problem then results in the scrubber where, at reduced pH (around 6.5), aluminum in the regenerated liquor precipitates out of solution as a silica-alumina complex. To alleviate this problem, the normal operating pH set point in the reactors was lowered to 9.0 from the original design condition of 11.0.

Since aluminum scaling was a concern early in the commercial lime test and mechanical problems occurred later, the dual alkali system was not operated for a sufficient period at high pH and full load to evaluate the effects of high pH on liquor flow rates and the subsequent longer settling time in the thickener.

## 6.2 RATE AND CONTROL OF REGENERATION REACTION

As expected, the reaction between the commercial lime and scrubber bleed was very rapid. Most of the pH change occurred in the primary reactor, and much less reaction (about 0.5 ΔpH) took place in the thickener. This faster reaction rate together with the better quality and higher concentration of lime solids in the lime slurry feed tank (35 to 40% vs. 20 to 30% for carbide lime) allowed better control of both the reactor system and the water balance.

## 6.3 REACTOR SOLIDS SETTLING

With the exception of one extremely high settling rate measured by Bechtel at the very beginning of the commercial lime testing (>33 ft/hr), the reactor solids settling rates obtained with commercial lime hydrate were not significantly different from those obtained with carbide lime. (Typical settling rates for carbide lime are around 13 to 20 ft/hr.)

## 6.4 FILTRATION OF REACTOR/THICKENER SOLIDS

One potential benefit expected with commercial lime was a higher filter cake solids content, with lower residual sodium because of enhanced cake washing. Unfortunately, there was no significant improvement in the filter cake insoluble solids, even under controlled filter conditions. In addition, the proper cake thickness (1/4 to 3/8 in.) could not be adequately maintained because the higher density solids generated by commercial lime made it difficult for the operators to control the filter tub liquid level, drum speed, and suspended solids concentration to the filter. Since the proper cake thickness could not be maintained, sodium losses during the commercial lime test did not differ significantly from those encountered with carbide lime. Under controlled filter operating conditions, however, considerably lower levels of residual sodium are possible.

# 7.0 REVIEW OF CAPITAL AND OPERATING COSTS

Capital and operating cost estimates for the LG&E dual alkali FGD system were developed during Phase I of the demonstration program. These estimates are summarized below and compared with the actual costs incurred at completion of construction and throughout the demonstration program.

## 7.1 CAPITAL COSTS

Installation of the dual alkali system at Cane Run Unit 6 required capital investment in three different subsystems: FGD, lime slurry feed, and waste processing and disposal. Each subsystem involved independent design and installation efforts, and the associated costs are presented by system in Table 7. The costs shown are reported on an as-incurred basis and thus do not represent a constant dollar value of the capital investment.

The actual capital investment of $19.5 million is somewhat higher than the originally estimated $17.0 million (excluding spare parts and working capital) (2). The material costs for the FGD system and the field supervision are slightly above the original estimate, while erection labor/overhead and the sludge disposal system are nearly double.

## 7.2 OPERATING COSTS

Table 8 presents the actual operating cost for 12 months of the demonstration program. Actual annual operating costs for the dual alkali system were much higher than estimated, both in terms of total annual cost and mills per kWh. The estimated total annual operating costs was $5.1 million (with reheat) (2), compared with the $7.9 million actually incurred. The major reasons for this difference are higher labor, maintenance, and soda ash requirements as well as soda ash and fuel oil unit costs that are about twice those estimated.

TABLE 7. ACTUAL CAPITAL COST BREAKDOWN BY SUBSYSTEM FOR LG&E CANE RUN UNIT 6
($ 1977 - 1979)

| | | Erection Costs | | | Engineering Costs[a] | | |
|---|---|---|---|---|---|---|---|
| Subsystem | Material Costs[b] | Direct Labor | Field Supervision and Engineering | Construction Overhead | System Supplier | LG&E Consultant | Total |
| FGD | 10,183,200 | 2,386,400 | 277,900 | 1,373,000 | 1,144,200 | 980,700 | 16,345,400 |
| Lime Slurry | 460,600 | 118,300 | 9,100 | 112,000 | -- | -- | 700,000 |
| Waste Disposal | 1,673,100 | 385,900 | 32,400 | 398,400 | -- | -- | 2,489,800 |
| Total | 12,316,900 | 2,890,600 | 319,400 | 1,883,400 | 1,144,200 | 980,700 | 19,535,200 |

---

[a] Owner's engineering is included in field supervision and engineering.

[b] Includes spare parts at 1% of total costs.

### TABLE 8. ACTUAL AVERAGE ANNUAL OPERATING COSTS (WITH REHEAT) FOR DUAL ALKALI AT THE LOUISVILLE GAS AND ELECTRIC COMPANY[a] (May 1, 1980 -- April 30, 1981)

| Direct Costs: | Quantity | Unit Cost, $ | Total Costs, $ |
|---|---|---|---|
| Carbide Lime | 44,647 ton | 15.32/ton | 683,992 |
| Soda Ash | 5,438 ton | 134.53/ton | 731,574 |
| Fuel Oil | 1,204,279 gal. | 1.02/gal. | 1,228,365 |
| Electricity | 12,925,000 kWh | 0.012/kWh | 155,100 |
| Water | 79,170,000 gal. | 0.05/1,000 gal. | 3,960 |
| Sludge Removal (Trucking & Landfill) | 117,890 ton | 2.50/wet ton | 294,725 |
| Maintenance Materials | 4.2% of total materials cost | | 520,510 |
| Labor | | | |
| Operation | 90,774 hr | 8.45/hr | 767,040 |
| Maintenance | 73,940 hr | 8.55/hr | 632,190 |
| Analysis | 2,080 hr | 12.00/hr | 25,000 |
| Supervision | 2,080 hr | various | 50,000 |
| Total Direct Costs | | | 5,092,456 |
| Indirect Costs: | | | |
| Overhead (Payroll & Plant) | 52.9% of 1,399,230 (Total Labor) | | 740,190 |
| Interest | 6.125% of 19,535,000 | | 1,196,520 |
| Depreciation | 4.65% of 19,535,000 | | 908,380 |
| Total Indirect Costs | | | 2,845,090 |
| Total Annual Operating Cost, $ | | | 7,937,546 |
| Mills/kWh | | | 7.0 |
| ¢/$10^6$ Btu | | | 70.4 |
| $/ton of S Removed | | | 498.8 |

[a] Basis: 300 MW (gross peak capacity) existing coal fired plant, 44% load factor, 9,960 Btu/kWhr, 3.5% S in coal, 91.6% $SO_2$ removal, average $SO_2$ removed -- 279 lb/min. at 300 MW (gross peak) load, on-site solids disposal by trucking after treatment, stack gas reheat 50°F.

Of the \$2.8 million differential, \$600,000 is because the soda ash makeup requirement was about triple the consumption estimated, and the soda ash cost was about double the estimated unit price. Around \$400,000 of the differential is due to reheater fuel oil at a unit cost more than double that in the estimate (\$1.02 per gal. vs. \$0.43 per gal.). Maintenance materials ran 4.2% of total system materials cost, compared to the 2.5% used in the Phase I estimate. This accounted for another \$240,000. Operating and maintenance requirements were more than triple those estimated (164,000 hours vs. 52,000 hours). This represents a \$1.4-million difference in operating cost.

The greatest requirements for operating labor are two to three men per shift for FGD sludge treatment, about two men per shift for the lime slurry system, with one to two men per shift each for instrumentation (control room), filter operation, and miscellaneous. Total operating labor amounted to an average of about 10 men per shift. Total maintenance labor requirements were equivalent to about eight men per shift, with the largest portion of this requirement for instrument maintenance.

Finally, slightly increased indirect costs for interest and depreciation (\$300,000) on the higher capital investment represent most of the remaining difference between estimated and actual operating costs.

Operating cost is much higher (7.0 vs. 3.2 mills/kWh), not only as a result of the increased annual operating cost, but also because the total power generated over the year was equivalent to a load factor of only 44% compared with a projected load factor of 60%.

## 8.0 REFERENCES

1. Van Ness, R. P., N. Kaplan, and D. S. Watson. "Dual Alkali Demonstration Project Interim Report," in Proceedings: Symposium on Flue Gas Desulfurization - Houston, October 1980; Volume 1, EPA-600/9-81-019a (NTIS PB81-243156), April 1981.

2. Van Ness, R. P. et al. Full-Scale Dual Alkali Demonstration System at Louisville Gas and Electric Co. - Final Design and System Cost, EPA-600/7-79-221b (NTIS PB80-146715), September 1979.

# DOUBLE ALKALI FLUE GAS DESULFURIZATION RETROFIT ON AN INDUSTRIAL COGENERATION FACILITY

BY: D. V. Francis
ARCO Chemical Company
A Division of Atlantic Richfield Company
Beaver Valley Plant
Monaca, PA 15061

R. J. Biolchini
and J. D. Coons
FMC Corporation
Air Quality Control Operation
231 North Martingale Road
Schaumburg, Illinois 60194

## ABSTRACT

This paper presents an operational review of the Double Alkali flue gas desulfurization system at an ARCO Chemical facility in Monaca, Pennsylvania. The FGD system was retrofitted to three pulverized coal-fired boilers burning high-sulfur coal (2.5 - 3.5%). The review discusses alternatives considered during the selection process, the system design, performance test results, system operations, and system availability. The system has met the Pennsylvania Department of Environmental Resources Emission requirements of 0.75 lbs $SO_2$/MM Btu and has met all the contract performance guarantees. Performance tests have demonstrated collection efficiencies up to 93%. During the past year, system availability has been above 97%. The filter cake which is mixed with fly ash to obtain a stabilized waste product has been easily handled, and landfill management results have proven better than anticipated. See Figure 1.

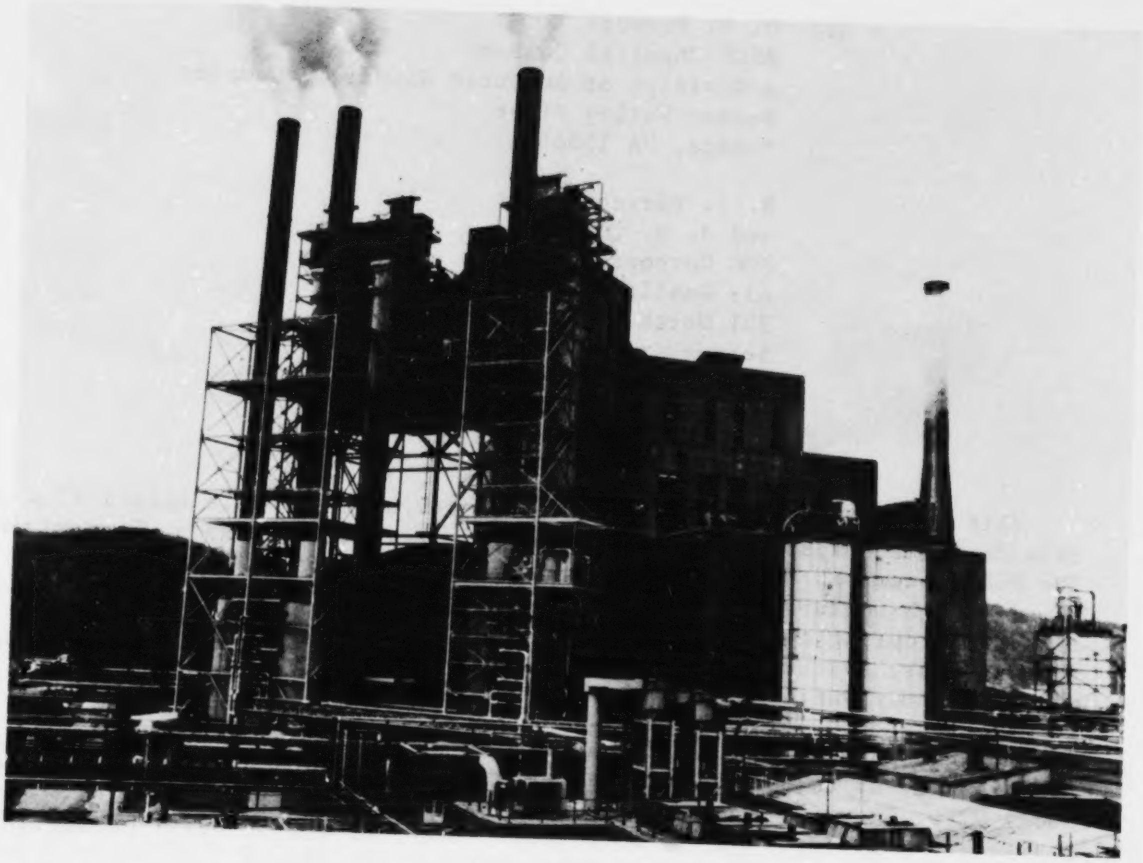


Figure 1. ARCO Chemical Company's Beaver Valley Plant

## PROCESS SELECTION

In response to the 1970 Clean Air Act, the Pennsylvania Department of Environmental Resources (PADER) in 1971 developed a state implementation plan (SIP) which required 80 to 85 percent of the $SO_2$ to be removed from the Beaver Valley area. The ARCO Chemical Beaver Valley plant in Monaca, Pennsylvania was burning high sulfur coal in coal-fired boilers. Therefore in 1971 ARCO Chemical began negotiations with the federal Environmental Protection Agency (EPA) and the Pennsylvania Department of Environmental Resources to meet the requirements of the Clean Air Act and the SIP.

Simultaneously ARCO Chemical began a study to determine how best to meet the Pennsylvania SIP. Natural gas and low sulfur fuel oil were judged not to be economical alternatives in light of the likely provisions of the Energy Program under consideration in Congress at the time.

In-depth reviews were conducted for (1) switching to low sulfur coal and (2) maintaining high sulfur coal with the addition of flue gas desulfurization.

Of the flue gas desulfurization technologies that were studied for their commercial viability and retrofit adaption only four warranted in-depth study.

(1) Citrate process with sulfur byproduct
(2) Lime/limestone process with throwaway sludge
(3) Sodium double alkali process with throwaway sludge
(4) Sodium absorption process with sulfuric acid byproduct

After further study the citrate/sulfur process was rejected due to insufficient experience with operation and economics of the system. The lime/throwaway sludge systems were also rejected due to the poor system availability that was being encountered as a result of the scaling/plugging of absorption equipment. In addition the review showed that the as produced sludge required further processing to make it handleable for waste disposal.

In 1975 and 1977, ARCO Chemical contracted with a sodium recoverable process supplier and a sodium double alkali process supplier respectively to develop definitive capital cost estimates.

After evaluating each proposal technically and economically, and after visiting an operating commercial installation of each, ARCO Chemical selected the FMC Double Alkali process over the recoverable process for the following reasons:

(1) Considerably lower capital
(2) Lower operating costs
(3) Less sophisticated process/operation
(4) More and longer successful demonstration
(5) Ease of retrofit

## RETROFIT CONSIDERATIONS

Retrofitting a flue gas desulfurization system to an existing facility often entails special problems which a grass roots application does not experience. The major problems which were encountered were:

(1) Space and access limitation
(2) Existing equipment interferences
(3) Electrostatic precipitator design constraints
(4) Booster fan interfacing
(5) Waste product disposal

### SPACE AND ACCESS

Space for the flue gas desulfurization system for all three boilers was limited to an area of 23,850 sq ft as outlined in figure 2. The area was further limited by the requirement that primary access to the boiler house was maintained as noted in figure 2. The FMC Double Alkali process which allows the regeneration and reagent storage equipment to be located remote from the absorption devices enabled the FGD system to be installed in the limited area while maintaining good access to the boiler house and FGD equipment.

### EXISTING EQUIPMENT INTERFERENCES

Existing equipment, material and structures in the absorption area had to be dealt with to achieve the area outlined in figure 2. The problems encountered and solutions were as follows:

(1) An existing sump which handled process effluent was demolished and a new one built in an adjacent area.

(2) An existing firehouse was relocated to an adjacent area.

(3) High voltage cables housed in fiber conduits with an unreinforced concrete casing interfered with normal foundation design and installation. Due to the high relocation costs the power lines

were not relocated. The foundations were designed to use auger cast piles which were placed between the conduits in such a manner as not to put any stress on the concrete casing for the conduit. The auger cast piles were also used due to the low bearing strength of the soil in the absorption area.

## ESP DESIGN CONSTRAINTS

The electrostatic precipitator was installed as retrofit to the boilers in 1968. The structure design limitations and the location of the ESP presented special retrofit problems. The ESPs are located above the boiler house with an outlet stub stack at 200 ft above grade. With a tie in point for the FGD system located at the stub stack, a ductwork-run to the booster fans at grade of approximately 200 ft was necessary.

The ESP also had structural design limitations of -1.0 inch w.g. to +6.0 inch w.g. The negative 1.0 inch w.g. required a specially designed barometric damper to be installed in the existing precipitator stack. The damper design is outlined in the system description. One good feature that has resulted from the precipitator's being located at a point above the boiler house and surrounding structures is that the existing stub stacks could be used for emergency bypass operations.

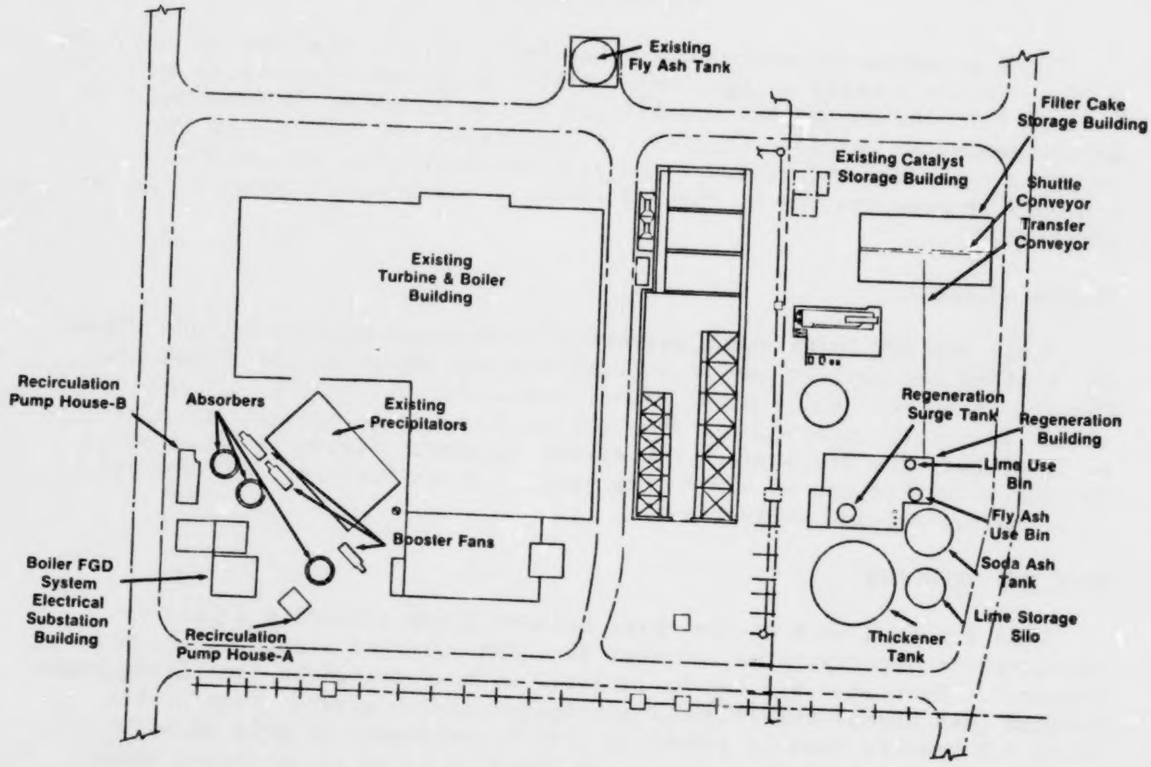


Figure 2. Site plan, ARCO Chemical Company's Beaver Valley Plant, Monaca, PA.

## BOOSTER FAN INTERFACING

Due to the design capability of the existing boiler fans a booster fan was required for each FGD system. In order to achieve efficient and safe boiler and precipitator operation, the two fans were linked together so that the booster fan would follow closely the main boiler fan. A feed forward signal is transmitted from the boiler ID fan, and a pressure signal is transmitted from the precipitator outlet to a signal conditioner/controller which modifies the absorber booster fan speed. Interaction between the fans has been very good.

## WASTE PRODUCT DISPOSAL

Waste product disposal at an existing facility can often represent a problem area. A disposal site remote from the plant was required; this dictated a process that would generate a waste product which could be transported over public highways. In addition, fly ash disposal was presenting a problem due to the dusting in transit and at the landfill areas. Although the FMC double alkali waste product can be disposed of directly, the mixing of the waste product with fly ash has solved the fly ash dusting problem while improving the landfill management operations.

# SYSTEM DESCRIPTION

FMC's patented concentrated double alkali process that was selected for sulfur dioxide control at the Beaver Valley plant was required to meet the code of 0.75 lbs $SO_2$/MM Btu established by the Pennsylvania Department of Environmental Resources. Figures 1 and 4 present an overview of the scrubber equipment and regeneration area respectively. Figure 3 is a schematic representation of the FGD process, and figure 2 shows a plan of the site.

## DESIGN CRITERIA

Three 300,000 lb/hr steam pulverized coal-fired boilers provide steam for heating and process use as well as electric power generation at ARCO Chemical's Beaver Valley plant. Coal containing up to 3.0% (dry basis) sulfur is burned, producing a flue gas sulfur dioxide concentration as high as 1,900 ppm on a dry basis. FGD system equipment sizing is based on 165,000 acfm flue gas at 425°F from each of three boilers, and 5200 lb/hr total sulfur dioxide collection.

## FLUE GAS HANDLING

Flue gas from each of the three boilers flows through a separate electrostatic precipitator, booster fan, and absorber module as shown in figure 3. Each absorber can be isolated with a seal-tight isolation damper located just beyond the original precipitator stub stack. Each of the three FGD booster fans is driven by a 400-horsepower variable speed DC motor and is capable of providing 165,000 acfm at up to 11 inches water gauge pressure. Booster fan speed is controlled by the boiler ID fan speed and trimmed with a precipitator outlet static pressure signal. Flue gas leaves the booster fan at approximately 400°F and enters the absorber where it is saturated and cooled to 135°F. A hot air injection-type reheater is provided, capable of heating 125,000 acfm saturated flue gas at the absorber exit to 160°F. A 150-foot insulated FRP stack is situated atop each reheat mixing chamber. An interesting feature of the gas handling train is the barometric damper (figure 5) which has been installed in the precipitator stubstacks. The purpose of the barometric damper is to maintain constant pressure in the precipitator to protect its structural integrity. The damper consists of two free-floating vanes with one counterweighted to open at plus two inches water gauge pressure and the other weighted to fall open at minus one inch water gauge vacuum. During normal operation, the precipitator outlet is maintained at 0 to .25 inches water gauge and both vanes are closed. In case of high or low pressure upset at the precipitator, the pressure or vacuum vane opens automatically to vent flue gas or allow air to enter until conditions stabilize.

## SULFUR DIOXIDE ABSORPTION

In the double alkali process (figure 3), sulfur dioxide is absorbed according to the following reaction:

$$Na_2SO_3 + SO_2 + H_2O \longrightarrow 2NaHSO_3 \quad (1)$$

sodium sulfite + sulfur dioxide + water    sodium bisulfite

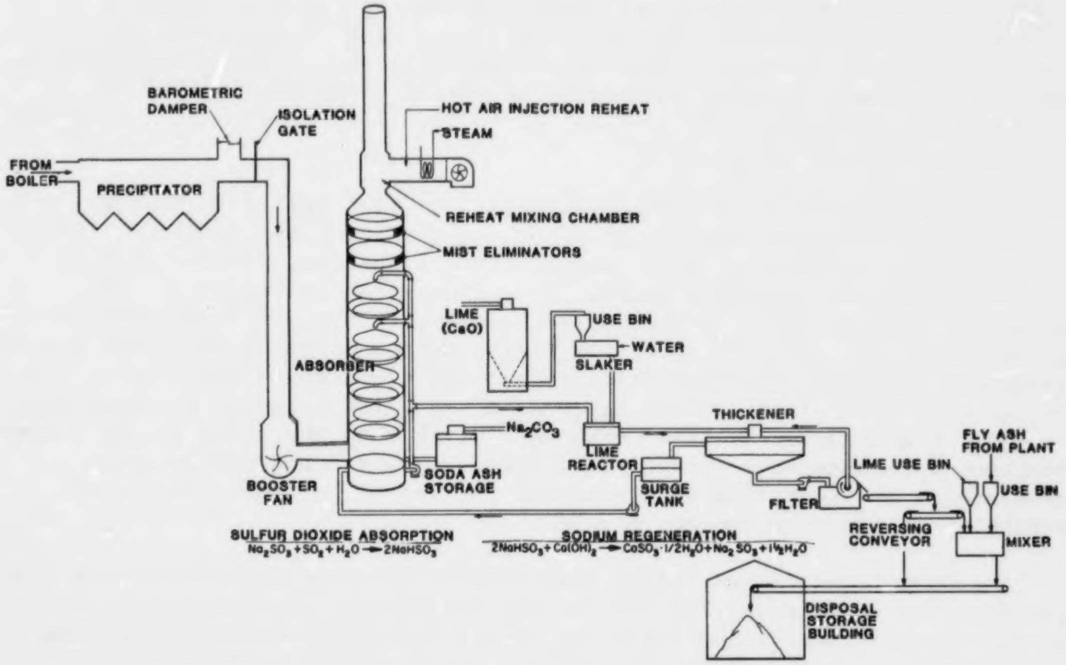


Figure 3. Flow Diagram of FMC double alkali FGD system at ARCO Chemical plant, Monaca, PA.

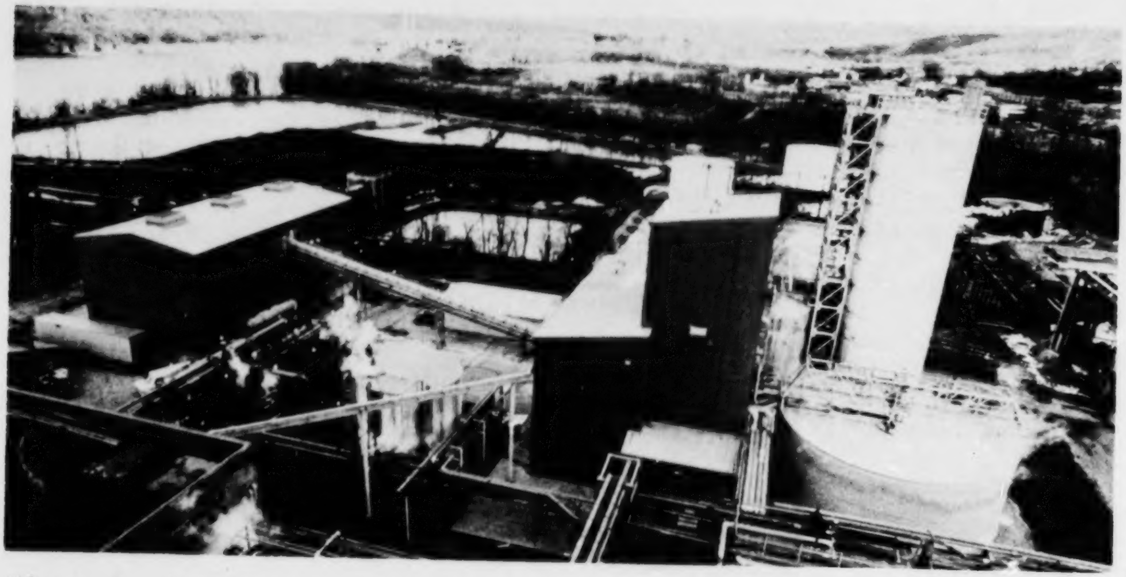


Figure 4. Regeneration section.

The pH of the scrubbing solution is controlled at 6.5. At this pH, the scrubbing solution contains equimolar concentrations of sodium sulfite and sodium bisulfite. This equimolar solution is highly buffered and can accept rapidly changing flue gas inlet conditions caused by swings in boiler load and/or changes in coal composition without upsetting the process control. As sulfur dioxide is absorbed, the ratio of bisulfite to sulfite increases, causing a decrease in pH. A bleed stream from the absorber recirculation loop is directed to the lime reactor which maintains the scrubbing solution pH at 6.5.

Each absorber is 17.3 feet in diameter, 65 feet tall from base to reheat chamber bottom, and designed for a superficial gas velocity of 9 ft/sec. The internals of this counter-current absorber consist of four stages of disc and doughnut baffles, as illustrated in figure 3. The vessel is constructed of carbon steel, lined with a glass-flake-reinforced polyester resin, with the exception of the bottom doughnut and inlet plenum which are constructed of Hastelloy G for high temperature protection. The bottom five feet of the vessel serve as an integral sump for the scrubbing liquor. The absorber is lined with acid brick from the floor to the bottom doughnut for temperature protection. Two stages of chevron-type mist eliminators are installed at the top of the vessel to remove entrained scrubbing liquor from the gas stream.

A rubber-lined recirculation pump (figure 6) draws liquor from the sump and delivers it to either of the top two stages. It also provides a bleed stream to the regeneration area. A full-flow standby recirculation pump is provided for each absorber. The recirculation system is designed to provide an L/G of 10 gal/1000 acf. Bleed flow rate is controlled to maintain a constant absorber sump level. Recirculation liquor pH is

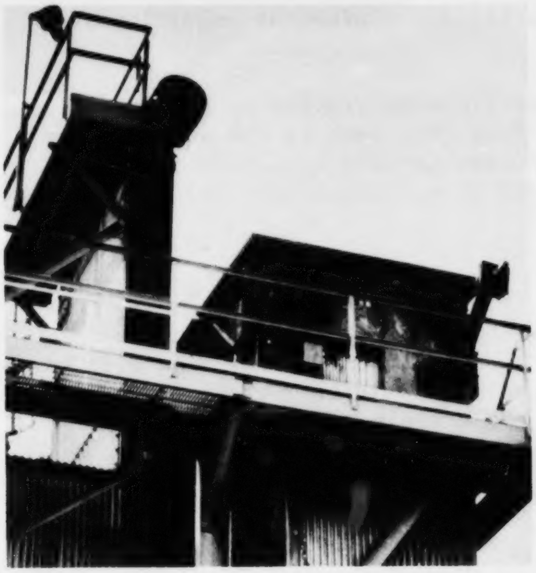


Figure 5. Barometric Damper.

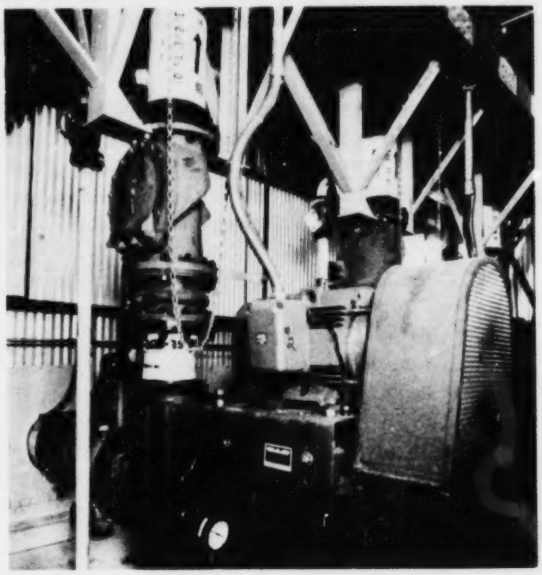


Figure 6. Recirculating pump.

controlled at 6.5 by addition of high pH regenerated liquor to the scrubber sump. All recirculation and bleed piping is constructed of fiberglass-reinforced polyester designed for corrosion and abrasion resistance.

REGENERATION

Sodium bisulfite in the bleed stream is reacted with slaked lime to precipitate calcium sulfite as well as regenerate sodium sulfite for use in the absorber according to the following reaction:

$$2NaHSO_3 + Ca(OH)_2 \rightarrow CaSO_3 \cdot 1/2\ H_2O + Na_2SO_3 + 1\text{-}1/2\ H_2O \qquad (2)$$

sodium bisulfite + calcium hydroxide
calcium sulfite + sodium sulfite + water

The regeneration is accomplished in a low-residence-time, continuously stirred tank reactor which is controlled at a pH of 8.5. The sensitivity of the pH control system is set to result in effectively stoichiometric consumption of lime.

Slaked lime is added to the reactor tank as 15% slurry which reacts with the bleed. Two immersion-type pH electrodes (one is a spare) measure and control the lime reactor overflow pH by controlling the pebble lime feed rate to the slaker.

The 1 to 1.5% calcium sulfite suspension formed in the lime reactor overflows to a 55-foot thickener tank (figure 7), where gravity settling of the solids occurs.

The thickener rake is equipped with an automatic power lift mechanism which is triggered by a high rake torque signal. Thickener underflow is concentrated to 15 to 30% solids.

The clear overflow from the thickener flows by gravity to a surge tank. The regenerated liquor is pumped from this tank to the absorbers on pH demand by a centrifugal pump which is complemented by a 100% installed spare. System water balance is maintained by a level controller and water addition valve at the surge tank.

## LIME CHEMICAL ADDITION

Pebble lime is delivered to the plant by self-unloading pneumatic trucks and stored in a 26-foot-diameter by 90-foot-tall silo. The silo has approximately 30 days storage capacity at the normal lime usage rate. Pebble lime is transferred to either of two use bins which are situated directly above two paste-type slakers by a pressure pneumatic system. A belt feeder transfers lime from the use bin to the slaker (figure 8) where it is hydrated in preparation for reactor tank addition.

## SODA ASH ADDITION

Soda ash is added to the FGD system to replenish sodium lost as entrained sodium sulfite and sulfate in the disposed filter cake. the 30-day soda ash supply is stored in a unique wet system. It is delivered to the plant site by rail car and transferred to a 30-foot-diameter by 30-foot-high storage tank (figure 9) by a pneumatic unloading system. As soda ash enters the tank it is wetted with a recirculating liquid stream. This intimate contact of the incoming soda ash with solution recirculated from the storage tank enables hydration of the soda ash to form a sodium carbonate solution. The soda ash solution eventually becomes saturated, and further unloading of dry soda ash results in the formation of a crystalline sodium carbonate monohydrate bed at the bottom of the storage tank. Saturated soda ash solution is drawn from the bottom of the storage tank, through the crystal bed, and is pumped to the surge tank.

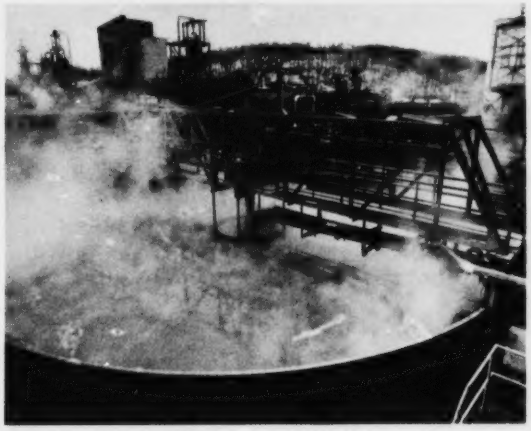


Figure 7. Thickener tank.

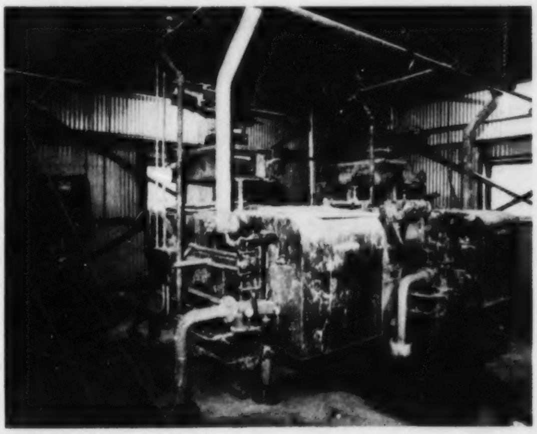


Figure 8. Lime slaker.

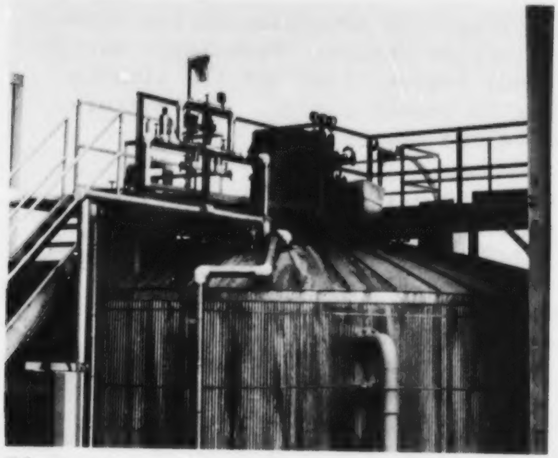


Figure 9. Soda ash storage tank.

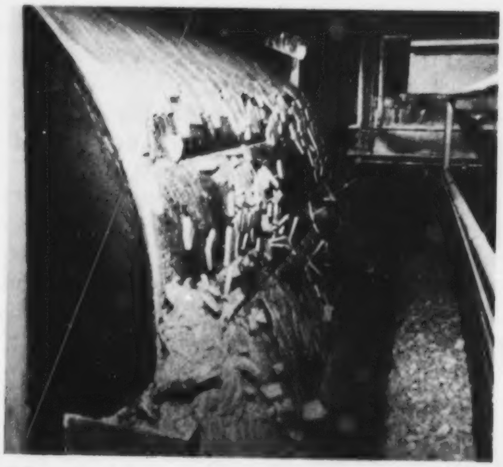


Figure 10. Vacuum filter.

## FILTER CAKE DEWATERING

Two rotary drum vacuum filters (figure 10), each capable of treating 100% of the calcium sulfite produced at design $SO_2$ collection, comprise the sludge dewatering equipment. Thickener underflow is pumped to the filters by air-operated diaphragm pumps. There are two full-flow underflow pumps for each filter. The 15 to 30% solids underflow is dewatered to a 50 to 55% solids filter cake on the knife- discharge-type rotary filters. The filter cake is washed with warm water, utilizing a wash belt compression roller assembly in order to enhance sodium recovery. Filtrate is returned to the thickener tank.

## STABILIZATION AND DISPOSAL

The Double Alkali FGD system produces a waste material of 50 to 55 percent solids which can be disposed of directly or mixed with fly ash. The final waste produced can be conveyed or handled without major difficulty.

Filter cake discharged from the rotary filters is transported by belt conveyors to a pug mill, where fly ash and pulverized pebble lime can be added to form a stabilized or fixated end product. Figure 11 shows the pug mill, equipped for adding fly ash and lime. The addition of these materials to the filter cake improves the engineering properties and handleability of the mixture two ways. First, an immediate percentage moisture reduction is accomplished by the addition of fly ash, thereby improving handleability of the mixture the instant it exits the mixer.

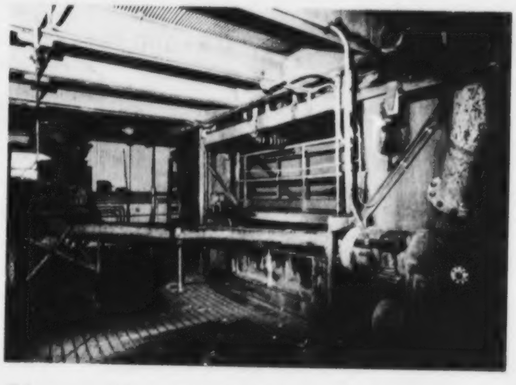


Figure 11. Pug mill.

Second, with the addition of lime, a long-term cementing action between the lime and fly ash known as pozzolanic action begins. Pozzolanic action is actually the formation of chemical bonds between lime and the alumina and silica components of fly ash, similar to cement curing. The mixture strength increases over a period of one to two months.

Fly ash and lime are added to the mixer in direct proportion to the filter cake feed rate, which is detected by a belt conveyor load cell. During normal operation, all of the fly ash and filter cake produced at the ARCO Chemical installation can be utilized effectively in the cake-ash mixer. The mixer can be bypassed by means of a reversing conveyor and the filter cake disposed of without stabilization if desired.

The stabilized mixture, or unmixed filter cake in the case of mixer bypass, is transported by an inclined belt conveyor from the mixer area to a disposal storage building, where it is allowed to accumulate. A front-end loader fills 20-ton standard dump trucks with the filter cake or mixture for transportation to a landfill disposal site approximately 15 miles from the plant. Mixing of the fly ash and filter cake was designed first to eliminate a fly ash dusting problem during transportation and at the disposal site and second to improve the waste product strength and handleability.

## LANDFILL

The disposal site, which was previously a strip mine, was designed to handle 240 tons per day of stabilized mixture for two and one half years. The landfill area was permitted for disposal of unmixed cake, fly ash, bottom ash and fly ash filter cake mixture. Site preparation as shown in figure 12 consisted of: (1) grubbing away of existing trees, (2) excavation of soil to increase capacity and for use for final cover, (3) building of a sedimentation pond for pile runoff, (4) diversion of water shed drainage around site, (5) building of a retention dike for waste product, (6) lining site with bottom ash for any leachate drainage, (7) installation of four monitoring wells (1 up gradient and 3 down gradient) for detection of ground contamination. In addition, a clay liner was installed in the

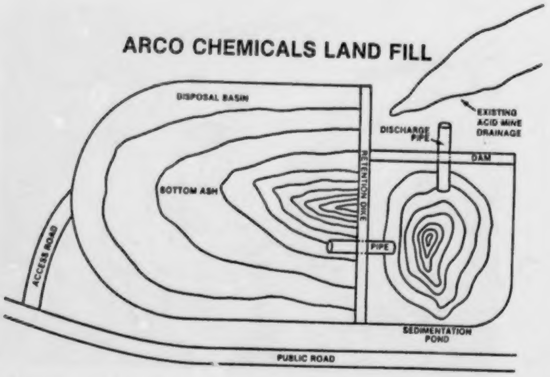


Figure 12. Plan of landfill area.

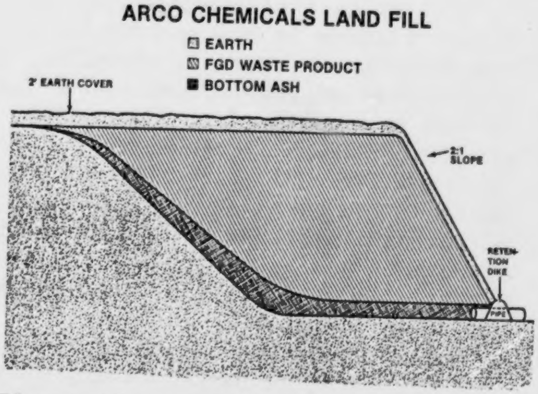


Figure 13. Landfill area elevation.

Figure 14. Dump truck at landfill.

Figure 15. Waste product.

sedimentation pond to prevent contamination of the pond by an existing acid mine drainage below the sedimentation pond. Although the site has an NPDES (National Pollution Discharge Elimination System) permit from the Pennsylvania Department of Environmental Resources which allows release of site runoff into existing streams, the sedimentation pond was sized to handle normal runoff for the life of the disposal site. The waste product to be landfilled is alkaline in nature with a pH between 8.5 and 11.0.

Site management called for the material to be placed in two-foot lifts and, as shown in figure 13, the landfill will have a final slope of 2 to 1. Final cover will be a two-foot earth layer.

## SYSTEM PERFORMANCE

### LANDFILL OPERATION

When the FGD system was brought on-line in August, 1980, the cake/fly ash mixing subsystem which had been a project revision was not complete, therefore necessitating the direct disposal of filter cake at the landfill. The cake and fly ash were transported by truck to the disposal site and mixed by bulldozer. This mode of operation proved satisfactory during the period prior to on-line operation of the cake-fly ash mixing subsystem. The mixing subsystem was made operational in January of 1981. The normal mode or operation has been to mix the filter cake and fly ash in the pug mill. However, when problems have occurred, mixing at the disposal site has proved satisfactory. Due to the failure and repair of an existing fly ash storage silo, the mixing system was unable to obtain fly ash for mixing at the plant for a period from early July until mid-September 1981. Fly ash and cake were transported to the site separately and mixed by dozer at the site. Under both the normal and backup modes of operation, the transportation and disposal of the waste product have been better than expected. The mixed product has eliminated the dusting problem and has proved to be easier to handle than the fly ash. Although provision was made to add lime to further improve the product strength, experience has shown that lime addition is not necessary and normal operation is without any lime addition.

The site preparation was not completed when the FGD system startup was initiated, thereby necessitating modifications to the landfill management. Instead of placing the waste product in two-foot lifts, the product was end dumped as shown in figure 14 and pushed by a bulldozer into place. Placement and compacting by normal dozer operation has been sufficient to provide the necessary compression of the waste product for better than satisfactory landfill operation, as shown in Figures 15 and 16.

The above procedure has resulted in stable landfill meeting the two-to-one slope criterion as shown in figures 12 and 13. The cost of the landfill operation has been lower than expected. Review of the monitoring wells during the first year of operation has shown no indication of leaching or ground water contamintation. the monitoring well located in the sedimentation pond has shown no significant change.

Landfill runoff and leachate discharge to the sedimentation pond have been minimal. No discharge from the sedimentation pond has occurred during the past year, as expected.

## FGD SYSTEM AVAILABILITY

The FGD system startup was initiated when the boiler number two absorber was brought on-line on August 16, 1980. Startups of absorbers three and four were initiated on August 18 and 29 respectively. System operation was completely turned over to ARCO Chemical within ten days after startup, with FMC personnel remaining on site in a consulting capacity. FGD availability remained high throughout the fall and winter months. Due to a scheduled boiler outage for late August to retube the boiler, operation of absorber number two was ceased after a week online. During the period from initial operation until December 31, 1980, absorbers three and four, as well as the regeneration area, were in operation with the exception of a one week period for absorbers three and four. The downtime during this period was to add a second mist eliminator to correct a carryover problem that had been encountered. Boiler number two was brought back on-line in December following retubing.

The majority of startup problems were not involved with the basic FGD system and had little effect on its availability. System availability tracking began on January 1, 1981. The average availability of the three boilers for the period from January 1, 1981 through December 31, 1981 was 97.6 percent. Causes of system unavailability are outlined in Table 1.

## TABLE 1. SOURCES OF UNAVAILABILITY
## JANUARY 1, 1981 TO DECEMBER 31, 1981

| Unavailability Cause | Hours | |
|---|---|---|
| | Average | Total |
| Poor lime quality (Jan) | 96.3 | 289.0 |
| #4 Booster fan maintenance (Jan) | 3.6 | 11.0 |
| #3 Booster fan bearing high temperature (Feb) | 1.7 | 5.0 |
| #4 Malfunction of sump level controller (Feb) | 1.3 | 4.0 |
| #2 Fly ash pluggage of demister (March) | 24.3 | 73.0 |
| #3 Booster fan cooling system failure & maintenance (March, Sept. Oct. Nov.) | 44.0 | 132.0 |
| #4 Isolation damper (April & May) | 10.0 | 30.0 |
| #3 & #4 Opacity meter calibration (Oct.) | 19.7 | 59.0 |
| #2 Maintenance on high temperature alarms (July) | 1.3 | 4.0 |
| #4 Booster fan electrical (July) | 5.7 | 17.0 |
| #2 and #4 Misc. minor maintenance (Mar, June, Aug) | 4.3 | 13.0 |
| Total unavailable hours | 212.3 | 637.0 |
| Total hours in period | 8760.0 | 26,280.0 |
| Availability | 97.6 | 97.6 |

Poor quality lime coupled with low water supply temperature forced the FGD system to be unavailable for operation for approximately four days during January. Proper lime slaking did not occur during this period when a lime with a lower than specific reactivity was slaked with water at temperatures below 35°F. As a result of the poor slaking, the slakers became plugged and the system was shut down. Adjustments were made to heat the water to 50°F, thereby permitting the use of the lower reactive lime.

System unavailability due to mechanical equipment problems has been limited to failure and corrective repair of the cooling fan for the booster fan motor of absorber three (132.0 hours in March) and electrical failure of isolation dampers on absorber four (30.0 hours in April and May).

Calibration of the opacity meter on boilers #3 and #4 have caused FGD unavailabilities of 3 hours and 28 hours respectively.

Pluggage of absorber #2 mist eliminators occurred in March and accounted for 73.0 hours of unavailability. The fly ash buildup was caused primarily by prolonged operation of the system with a precipitator which was malfunctioning.

Other occurrences that have taken the system out of service have been a plant utility failure, failure of an electrostatic precipitator, and outages to correct boiler problems.

Table 2 presents the monthly recorded availability per boiler. Availability is defined as the number of hours the FGD system is available for operation divided by the number of hours is the period.

TABLE 2. FGD SYSTEM AVAILABILITY
JANUARY 1, 1981 TO DECEMBER 31, 1981
(PERCENT)

| | UNIT 2 | UNIT 3 | UNIT 4 | UNIT AVERAGE |
|---|---|---|---|---|
| JAN | 87.3 | 86.8 | 85.1 | 86.4 |
| FEB | 100.0 | 99.3 | 99.4 | 99.6 |
| MAR | 90.2 | 85.6 | 99.7 | 91.8 |
| APR | 100.0 | 100.0 | 96.9 | 99.0 |
| MAY | 100.0 | 100.0 | 100.0 | 100.0 |
| JUN | 99.9 | 100.0 | 100.0 | 100.0 |
| JUL | 99.4 | 100.0 | 97.7 | 99.0 |
| AUG | 98.9 | 100.0 | 99.5 | 99.5 |
| SEPT | 100.0 | 98.6 | 100.0 | 99.5 |
| OCT | 100.0 | 94.4 | 96.2 | 96.9 |
| NOV | 100.0 | 99.2 | 99.9 | 99.7 |
| DEC | 100.0 | 100.0 | 100.0 | 100.0 |
| AVERAGE | 98.0 | 97.0 | 97.9 | 97.6 |

Overall, the system availability has been extremely high. If the occurence in January caused by poor lime quality were eliminated, system availability would have averaged about 98.7%. These high availabilities are expected to continue.

## PERFORMANCE TEST RESULTS

### SULFUR DIOXIDE COLLECTION

Sulfur dioxide collection efficiencies were determined utilizing both Pennsylvania Department of Environmental Resources (PADER) and EPA stack testing methods. The PADER method is more stringent than EPA Method 8 since it includes sulfur trioxide as a sulfur dioxide emission. PADER methodology was used for all official compliance testing.

Official PADER test results confirm that emissions from all three absrobers comply with the 0.75 lb $SO_2$/MM Btu emission limitation in the Pennsylvania code. In addition, sulfur dioxide collection efficiencies in the 86% to 93% range have been measured at various levels of recirculation pH and inlet sulfur dioxide concentration.

### PARTICULATE

Test results show that absorber emissions are meeting the 0.13 lb/MM Btu particulate code. Modified EPA Method 5 particulate tests have revealed absorber sodium emissions to be approximately 0.02 lb/MM Btu as sodium sulfate since the installation of a second mist eliminator. Since the absorbers are known to collect some fly ash, not net particulate addition has occurred.

## PRESSURE DROP

System gas side pressure drop was measured at 6.8 inches water gauge from the precipitator outlet to the absorber outlet at design gas flow rate.

## CHEMICAL CONSUMPTION

Filter cake analyzed for free lime has revealed less than 0.02% excess lime on a dry weight basis. This relates to a stoichiometric ratio of 1.001 for lime utilization. This does not include lime required for filter cake stabilization. Even lower excess lime consumption may be achieved by tighter lime reactor pH control and improved slaker operation.

Sodium consumption as a percentage of sulfur dioxide collected was determined by analyzing filter cake for sodium and total sulfur content. Sodium consumption was approximately 6.5% of the sulfur dioxide collected on a molar basis, corresponding to about 330 lb/hr soda ash usage at normal conditions. Filter cake analysis was the method used for determining chemical consumption since essentially all sulfur collected and soda ash added to the system exit via the filter cake at steady state conditions. Sodium consumption is kept minimal by avoiding costly spills in the absorber and regeneration areas. A favorable system water balance helps avoid tank overflows.

## POWER CONSUMPTION

FGD system power consumption has averaged about 1000 kilowatts during the first year and a half of operation. Roughly 90% of this total is consumed in the gas handling/absorber area. The total system power consumption corresponds to 0.7% of the rating of 150 MWe based on flue gas volume.

## FILTER CAKE SOLIDS

Filter cake discharge from the rotary filters has ranged from 47% to 60% solids. Filter cake moisture can be controlled to a large extent by the density of the thickener underflow slurry feed to the filters. Slurry density is controlled by the addition of fresh water to the thickener underflow. Thin slurry, consisting of roughly 10% insolubles, has provided better results than thicker slurries in the 20% to 30% insolubles range. this is due to the excellent control of filtering operation afforded by thin slurry

Filter cake consisting of roughly 53% solids seems to be optimum for disposal and handling purposes at the ARCO Chemical installation.

## CAKE/ASH MIXTURE STRENGTH

Mixtures of fly ash and filter cake, excluding lime, were collected from the ARCO Chemical pug mill. These mixtures were found to have an unconfined compressive strength of 1.18 tons/ft$^2$ after 28 days curing time due to pozzolonic action. With the lime addition, strengths greater than 12 tons/ft$^2$ are expected. This estimate is based on a recent study of various mixtures of fly ash, quicklime, and FMC double alkali filter cake.

## SUMMARY

Performance of the FMC Double Alkali FGD system has continued to meet the design and operating criteria established by ARCO Chemical during the proposal evaluations.

Performance test results have been better than the design criteria. System availability has continued to be high with an average for 1981 above 97 percent.

Reagent costs have been higher than anticipated due to higher than design excess air that has been experienced for the boiler operations. Corrective measures are under way to improve the boiler operations, and reagent costs are expected to decrease substantially.

The landfill operation has proved to be better than anticipated. Costs of waste product disposal have been lower than originally projected.

Figure 16. Another view of ARCO Chemical's landfill operation.

# PILOT TESTING OF LIMESTONE REGENERATION IN DUAL ALKALI PROCESSES

by: John C. S. Chang and J. H. Dempsey
Acurex Corporation
Research Triangle Park, NC 27709

Norman Kaplan
U.S. Environmental Protection Agency
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

## ABSTRACT

Major progress has been made on the technology of replacing lime with limestone as the regenerant for dual alkali flue gas desulfurization processes. Although previous attempts at using limestone as a regenerant have resulted in occasional production of nonsettling solids, this problem has been overcome during recent pilot testing. Operating parameters have been identified that have thus far permitted more than 2500 hours of operation without the previously encountered solids settling problem. Soda ash consumption rate has been reduced to less than 0.02 mole $Na_2CO_3$/mole $SO_2$ absorbed in recent pilot plant tests. Solids settling rate was maintained above 1.0 cm/min, and filter cake solids content was maintained between 45 and 75 percent with greater than 90 percent $SO_2$ removal and greater than 90 percent limestone utilization. Comparison of lime and limestone regenerated dual alkali systems indicates that the latter is not only technically feasible but also economically attractive.

# PILOT TESTING OF LIMESTONE REGENERATION IN DUAL ALKALI PROCESSES

## INTRODUCTION

The sodium-based dual alkali (DA) process is one of the available second generation throwaway wet flue gas desulfurization (FGD) technologies currently utilized in the United States(1). The DA process has the advantages of clear solution scrubbing, low liquid-to-gas ratio, and high reliability(2). All existing commercial-scale DA scrubbers use lime to react with spent scrubber effluent and regenerate the sodium sulfite scrubbing solution. Since lime is produced from limestone by an energy intensive calcination process, the direct use of limestone is increasingly more attractive with the rising cost of energy. In recent years, unit weight lime cost has been as much as 5 to 10 times the cost of limestone. It is estimated that a significant cost savings could be realized by converting a DA FGD system from lime to limestone.

EPA's Industrial Environmental Research Laboratory at Research Triangle Park, North Carolina (IERL-RTP) has sponsored a series of research projects to investigate the more advanced and more cost effective limestone DA FGD technology. Early laboratory and bench-scale studies indicated that within certain constraints, such as the use of finely ground limestone and long reactor residence time, limestone regeneration of dual alkali scrubbing liquor was technically feasible without inordinate increases in system complexity compared to lime systems. Control of several important parameters of system chemistry--such as total oxidizable sulfur (TOS = sulfite + bisulfite), sulfate, magnesium, iron, and the solid solution of calcium sulfite-sulfate--was identified as crucial to potential success of the limestone regeneration technique(3,4).

Prototype scale testing was conducted with a 20 MW facility at Gulf Power Company's Scholz Steam Plant to evaluate the commercial feasibility of the limestone regenerated DA process(5). The 20 MW Scholz test facility had been previously used to demonstrate lime DA and was recommissioned and modified for the limestone testing. Due to budgetary constraints, equipment problems, and other factors, only 2 months of testing were completed.

In general, the prototype system performed well. Sulfur dioxide removal efficiency in excess of 95 percent was achieved at times; typically, it was greater than 90 percent. Limestone utilization in excess of 97 percent was achieved. Process operability was very good, and the system was able to easily accommodate variations in inlet $SO_2$ concentrations of as much as 500 ppm by merely adjusting regenerated liquor feed rate.

The production of poor or non-settling solids was the most significant process problem identified. Solids content of the filter cake ranged between 35 and 45 percent, which was well below the anticipated 55 percent. At times, very fine, needle-shaped crystals with very low settling rates were produced. The thickener residence time was not sufficient to allow these solids to settle. Therefore, process interruptions, which occurred when the thickener overflow contained noticeable amounts (>1000 ppm) of finely suspended $xCaSO_4 \cdot yCaSO_3 \cdot zH_2O$ mixed crystal, could not be avoided. The soda ash consumption of 0.29 moles of $Na_2CO_3$/mole of $SO_2$ removed far exceeded the expected consumption rate of 0.05 moles $Na_2CO_3$/mole $SO_2$ removed observed in lime DA systems. A substantial portion of this consumption was due to leaks and other liquor losses in the system not related to the increased liquor losses associated with the poor quality filter cake.

Since the facility was not operated in the 4 year period between lime DA testing and the recent limestone DA test period, much of the equipment was in poor condition. In particular, the rotary vacuum filter did not operate properly during most of limestone DA testing and thus may have been responsible for much of the poor quality solids produced and the high soda ash consumption.

To support the prototype and future full-scale operation and to provide EPA with a versatile research tool, a 0.1 MW pilot-scale dual alkali system was established at IERL-RTP and testing was started in 1979. Acurex Corporation has been contracted by IERL-RTP since 1977 to conduct the DA pilot plant testing and to provide engineering service. The pilot plant successfully simulated the prototype-scale testing at the Scholz steam plant. With several minor system modficiations and careful process control, the non-settling solids problem was avoided and the IERL-RTP pilot plant successfully demonstrated long-term operability of the limestone regenerated DA process from April to July 1981. The following additional concerns were identified during this period of operation:

(1) High soda ash consumption rate: A soda ash consumption rate of 0.2 mole $Na_2CO_3$/mole $SO_2$ removed was obtained during pilot-plant long-term testing (0.05 moles $Na_2CO_3$/mole $SO_2$ might be expected). The high soda ash consumption rate was a result of excessive liquor loss and was compounded by the high TOS concentration in the scrubbing liquor and the high liquid content of the waste cake. The high liquor loss resulted from the small liquor inventory relative to the large sampling requirements of the pilot-scale research project and the high liquor content of the waste.

(2) Poor solids quality: During this period, the typical solids content in the filter cake ranged from 40 to 45 percent (55 percent was expected), and the TOS concentration in the liquor was maintained sufficiently high to ensure the production of settleable solids.

Both poor filter cake quality and high TOS level tend to increase the potential for excess sodium loss and reduce the economic feasibility of the system. From August 1981 to February 1982, additional pilot plant tests were conducted with the goal of improving the economic feasibility of the limestone regenerated DA system. The reactor system was modified and the scrubber operation mode was further refined with respect to previously defined operational constraints. Results from recent pilot plant testing indicate significant improvement in both filter cake quality and soda ash consumption rate. The objectives of this paper are to report highlights of pilot plant testing and to discuss recent developments in the limestone regenerated DA FGD process.

## TEST FACILITY

The pilot plant was operated as a sodium-based, concentrated-mode dual alkali system during the tests reported here. The absorber is a 23 cm (9 inch) diameter tray tower designed for 7.5 $m^3$/min flue gas capacity (0.1 MW). The overall process flow diagram is shown in Figure 1. Flue gas from an oil/gas-fired boiler is drawn through the absorption tower by an induced draft fan located immediately upstream from the stack. Gaseous $SO_2$ from cylinders is fed into the ducting before the absorber to spike the flue gas to predetermined concentrations of $SO_2$. The oxygen content of the flue gas is controlled by adjusting the boiler excess air. The absorber contains a spray section (quench) followed by three trays in series for gas/liquid contacting. The trays are sieve-type with 4.8 mm (3/16-inch) holes on a 9.5 mm (3/8-inch) triangular spacing. Design pressure drop across the trays is 20.3 cm (8 inches) of water. Regenerated absorbent liquor from the thickener hold tank is fed to the top tray and overflows a 1.3 cm (1/2-inch) weir into a collection box and then to successive trays via internal downcomers and weirs countercurrent to the flue gas flow. To prevent short-circuiting of gas around the trays, liquor from the bottom tray is collected in a weir box and overflows to the hold tank through a standpipe. Part of the liquor from the absorber hold tank is recycled to the spray for quenching the inlet gas. Provisions are included for recycling spent absorber liquor to the top tray for pH control which is important for lime dual alkali operation or for increasing the absorber L/G ratio. A bleed stream from the absorber recycle loop is sent to the reactor system for regeneration.

Two different reactor systems designed for lime and limestone regeneration, respectively, were installed as shown in Figure 2. The lime reactor system has the following features: (1) Two stirred tanks in series: one with a short-residence time (volume = 20 liters) is followed by a second tank with a longer residence time (volume = 150 liters). (2) Complete mixing flow patterns with gravity overflow through the reactors. (3) Each reactor is equipped with two overflow ports to allow for operation over a range of flow rates and reactor residence times. The limestone reactor system was modified to include the following features: (1) Three equal-sized tanks in series (110 liters each). (2) Initial plug-flow followed by complete-mixing flow patterns in each reactor. (3) Slurry is transferred from the plug-flow section to the completely mixed section by gravity underflow. (4) Agitator motion is in the direction to mix tank contents in an upward direction.

Provisions were incorporated for feeding reactant (lime or limestone) either as a dry solid or as a slurry. Dry solids may be fed from a screw feeder. Slurry is fed from a scale-mounted, agitated feed tank using a metering pump. During all of the testing described here, lime and limestone were fed as slurries. The feed rate can be manually set for either pH or reactant stoichiometry control. Reactor effluent slurry, containing 2 to 5 percent insoluble solids, flows by gravity to the thickener center well.

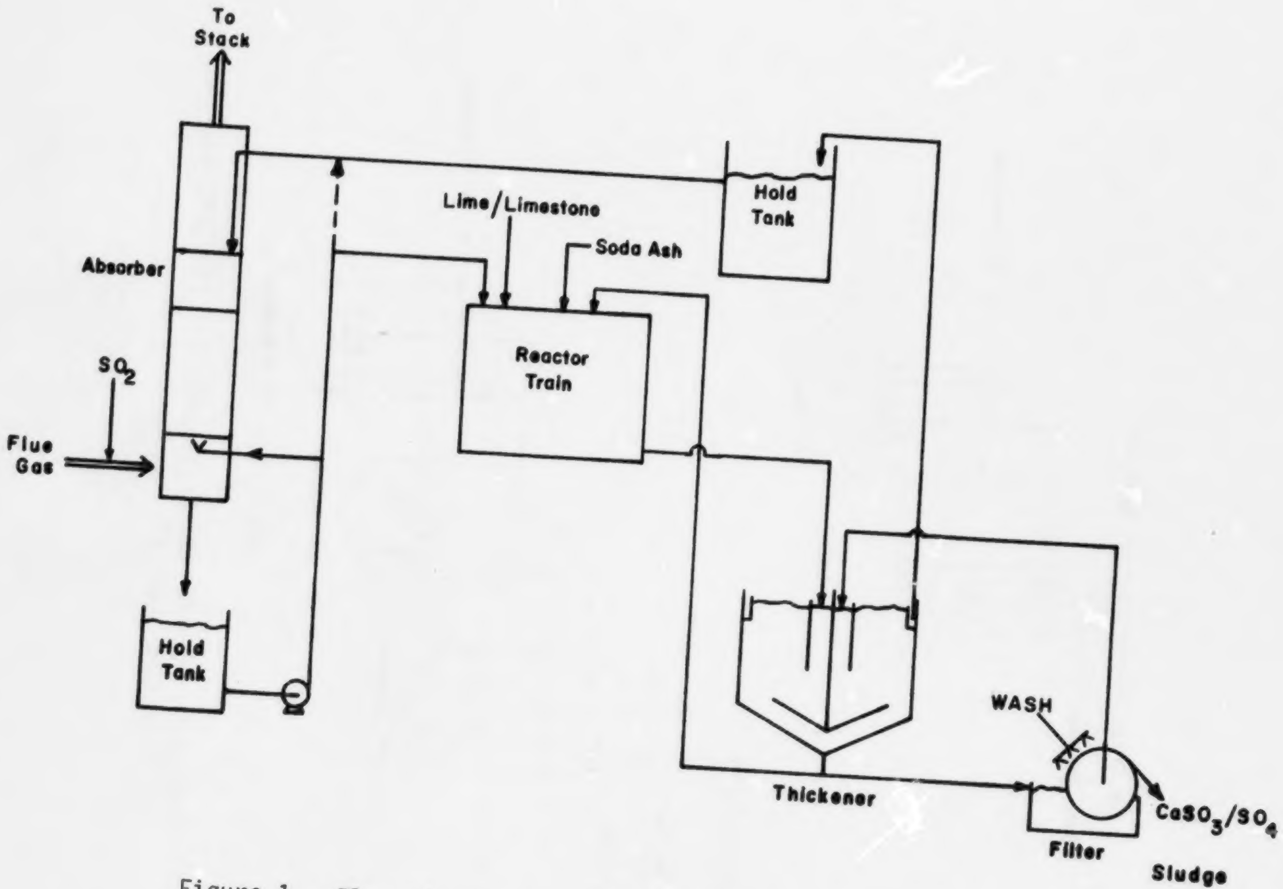


Figure 1. Flow diagram of EPA/IERL-RTP dual alkali pilot plant.

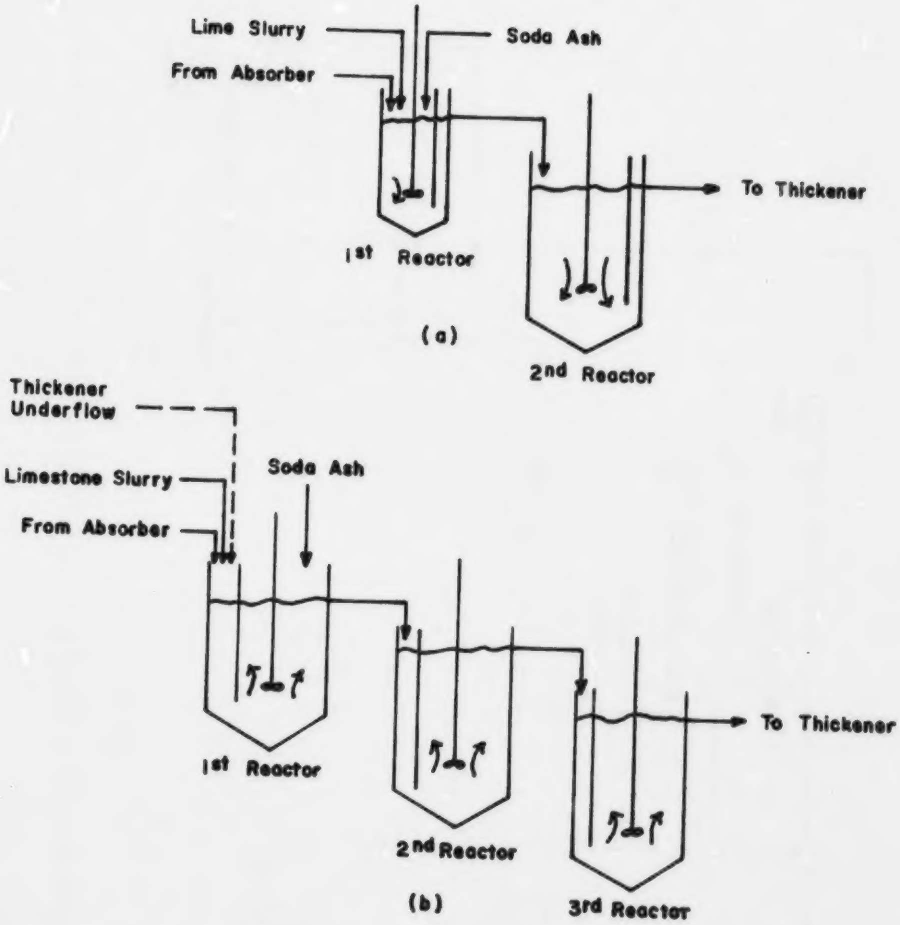


Figure 2. Schematic of the reactor systems for EPA/IERL-RTP (a) lime (b) limestone dual alkali pilot plant.

Clarified liquor, usually containing less than 0.1 percent insoluble solids, overflows from the thickener to the forward feed hold tank from which it is pumped to the absorber. Thickener underflow is pumped to a rotary drum vacuum filter. Overflow from the filter is returned to the thickener centerwell. The filter cake is washed using fresh process makeup water to recover occluded sodium salts. Mixed filtrate and wash water are returned to the thickener centerwell. The filter generally operates continuously except when the thickener underflow solids concentration drops below about 12 percent.

The pilot plant was operated at the conditions listed in Table 1 for about 100 hours per week. Scrubber performance and system conditions are established by logging operational data each hour. The gas-phase $SO_2$ concentration is measured continuously by ultraviolet spectrophotometry (DuPont 400 $SO_2$ analyzer) and checked by wet gas analysis. Liquid samples are taken regularly from the reactors and the thickener and separated into liquid and solid fractions by filtering under positive pressure. Chemical analyses to quantify total sulfur, TOS, alkalinity, carbonate, sodium, calcium, and magnesium were performed on liquid samples. Filter cake samples were taken daily for calcium, sodium, sulfur, and carbonate analyses to determine limestone utilization.

## TEST PROGRAM

Two phases of limestone DA tests are reported:

- High sodium consumption operation.
- Simulated low sodium consumption operation.

The high sodium consumption phase was planned to test the operability of the system at conditions that minimized the stresses expected during more normal operation. The system was not stressed by imposition of stringent water balance requirements, and the resultant high sodium consumption was accepted and accounted for. Encouraged by the high sodium consumption phase results, a minimum sodium consumption phase was started. During this low sodium consumption phase, the system was stressed by imposing a closed water loop (closed water loop implies only liquor lost that is associated with filter cake). Further stress was applied by simulating 100 percent return of soluble sodium by filter cake washing. Since 100 percent filter cake washing efficiency is not practical, the low sodium consumption phase represents the most stressful conditions anticipated for limestone DA systems with respect to water balance and sulfate accumulation. The two phases of testing described here should bracket actual normal-operation sodium consumption. Thus, if successful operation could be achieved in both phases, the viability of the limestone DA process would be shown.

Phase 1. High Sodium Consumption Operation: Soda ash was used as the only sodium additive fed to the scrubber system to make up sodium losses. Due to the research nature of the pilot plant test, liquor loss through sampling, maintenance, and filter cake entrained liquor losses was high compared to commercial expectation. It was estimated that more than 30 percent of the total liquor loss was not accounted for. Since all of the

TABLE 1. OPERATING CONDITIONS OF IERL-RTP LIMESTONE DUAL ALKALI PILOT PLANT

---

L/G ratio = 0.40-0.54 $\ell/m^3$ (3-4 gal./1000 acfm)
Liquid flow rate = 3.8 $\ell$/min (1 gpm)
Scrubber pressure drop = 15-18 cm (6-7 in.) of water
Flue gas oxygen = 11%
$SO_2$ feed rate = 2.7-3.2 kg/hr (6-7 lb/hr) (about 3000 ppm at scrubber inlet)
Reactor residence time = 90-100 min total
Reactor temperature = 32-43°C (90-110°F)
Limestone feed rate = 0.9-1.0 stoichiometry
Limestone used = 80% less 325 mesh Fredonia limestone

---

sodium lost (as $Na_2SO_3/Na_2SO_4/NaHSO_3$) was replenished with soda ash, the pilot plant data during this phase does not actually represent the most stringent conditions of operation of the dual alkali system. The operating advantage of this operational mode was low sulfate and impurity accumulation since the purge rate was relatively high. However, the excessive liquor loss rate increased the soda ash consumption rate and thus the expected operating cost.

Phase 2. Simulated Low Sodium Consumption Operation: To more closely simulate worst case operating conditions with best case environmental and economic conditions and maintain the same level of sampling and analytical data, sodium was added to the system as sodium carbonate, sulfite, bisulfite, and sulfate proportional to the concentrations of those ions in the scrubbing liquor. Thus, the excessive liquor loss was replenished by simulated scrubbing liquor, and the accumulation of sulfate ion due to oxidation was simulated while stressing the system to the utmost in terms of operation.

## RESULTS AND DISCUSSIONS

Three hundred hours of Phase 1 and 700 hours of Phase 2 operation were conducted in the pilot plant. For the convenience of discussion, the operating results are categorized into the following six areas for each phase:

(1) Sulfur dioxide absorption.
(2) System chemistry.
(3) Limestone addition.
(4) Sodium makeup.
(5) Regeneration.
(6) Filter cake quality.

## PHASE 1 - HIGH SODIUM CONSUMPTION OPERATION

All sodium losses were made up by sodium carbonate addition. Sodium consumption was greater than expected due to excessive loss of liquor and inability to efficiently wash filter cake.

(1) Sulfur dioxide absorption: Ninety to ninety-two percent removal of $SO_2$ was readily achieved at L/G ratios of 0.40-0.54 $\ell/m^3$ (3 to 4 gal./1000 acfm). The inlet $SO_2$ concentration was generally maintained at 3000 ppm.

(2) System chemistry: The pH values of regenerated scrubbing liquor (inlet to absorber) ranged between 6.4 and 6.6. The pH drop across the absorber ranged from 0.3 to 0.4; thus, spent scrubber effluent ranged from 6.0 to 6.3. The TOS was controlled at about 0.88 gmole/$\ell$ by adjusting the soda ash makeup rate. Total acidity analysis indicated that approximately 45 percent of the TOS was bisulfite. Therefore, the sodium sulfite concentration was estimated to be 0.5 gmole/$\ell$. In the DA process, $SO_2$ is absorbed according to following reaction:

$$SO_3^{=} + SO_2 + H_2O \longrightarrow 2HSO_3^{-} \qquad (1)$$

The mechanisms of $SO_2$ absorption and liquid reactions were analyzed by Chang and Rochelle, and a high ratio of $SO_3$ to $SO_2$ is required to ensure high $SO_2$ removal efficiency(6). At a ratio of 2.6 moles of sulfite per mole of $SO_2$ absorbed in the scrubbing liquor, 90 to 92 percent $SO_2$ removal was obtained during the test period.

Another important reaction is the oxidation of sulfite:

$$SO_3^{=} + 1/2\ O_2 \longrightarrow SO_4^{=} \qquad (2)$$

In steady-state operation, sulfate must be removed from the system as fast as it is formed. The sulfate ion, which is not active in absorbing sulfur dioxide, can be partially coprecipitated by reaction with dissolved limestone. Sulfate is also purged from the process through the entrainment of solution in the filter cake and miscellaneous liquor losses. The sulfate to TOS ratio in the scrubbing liquor was 0.5 during the Phase 1 operation. This was probably lower than expected in a commercial system due to the high sulfate purge rate associated with the excessive liquor losses.

(3) Limestone addition: The limestone was fed to the first reactor continuously as a 40 percent slurry of Fredonia fine grind (80% < 325 mesh) and fresh water. The feed rate was controlled at 0.9 to 1.0 stoichiometric ratio of moles of $CaCO_3$ fed per mole of $SO_2$ absorbed. Limestone utilization of 93 percent was obtained as calculated, based on filter cake analysis.

(4) Sodium makeup: A soda ash consumption rate of 0.13 moles of $Na_2CO_3$ added per mole of $SO_2$ absorbed was obtained. This was 35 percent lower than previous pilot plant tests and about 55 percent lower than the Scholz consumption rate. Actually, the soda ash consumption rate could be further decreased by reducing the sampling load, increasing cake washing efficiency, and tightening the water loop. Sodium sulfite was used to replace soda ash as the major source of sodium makeup for 140 hours during the test. Similar scrubber performance was obtained with both sodium sources. The data indicated that there was no difference between alkalinities or active sodium derived from carbonate or sulfite.

(5) Regeneration: Calcium sulfite is precipitated by reacting spent sorbent liquor with limestone to regenerate sulfite for use in the absorber according to the following overall reaction:

$$2HSO_3^- + CaCO_3 \longrightarrow CaSO_3\downarrow + SO_3^= + H_2O + CO_2 \qquad (3)$$

Most of the regeneration was accomplished in the first two reactors. Solids analysis showed that more than 60 percent of the limestone added was reacted in the first reactor and was accompanied by considerable bubbling, probably due to carbon dioxide evolution. Previously it was thought that an active sodium concentration of 1.8 gmole/ℓ was required to avoid production of non-settling solids by Reaction (3). The new data showed that, with the modified reactor system illustrated in Figure 2b, high quality calcium sulfite solids were produced at an active sodium concentration of 1.36 gmole/ℓ with an average 2.2 cm/min settling rate observed in the third reactor. The reduction of minimum active sodium level and the improvement in solid settling rate greatly lowered the soda ash consumption rate and enhanced system reliability.

A short-term test was performed at a lower active sodium level (0.69 gmole/ℓ), higher sulfate-to-TOS ratio (1.32), and shorter reactor residence time (60 minutes). System upset due to non-settling solids was encountered, and lower $SO_2$ removal efficiency (85 percent) was obtained. More tests were suggested to further investigate the effects of system chemistry and reactor configuration on limestone regeneration. However, the data to date indicated that system upset could be avoided and good quality waste solids produced by operating the system with the modified reactor system and with an active sodium level above 1.36 gmole/ℓ.

(6) Filter cake quality: Filter cake with 75 to 80 percent solids was produced when the reactor system was initially modified and sulfate-to-TOS ratio was low (0.47). This was considerably higher than the 40 to 45 percent obtained during previous tests before reactor modification. Solids analysis showed that sulfate was coprecipitated at a rate of 0.05 mole sulfate/mole sulfite. The sodium content in the thoroughly washed filter cake samples was about 5 mg Na/g dry cake. This indicated that a minimum soda ash makeup rate of 0.016 mole of $Na_2CO_3$/mole $SO_2$ absorbed would be required even with no liquor losses and 100 percent filter cake washing efficiency. Sodium coprecipitation and occlusion was the most likely cause of loss.

## PHASE 2 - SIMULATED LOW SODIUM CONSUMPTION OPERATION

Soda ash addition was reduced to a rate comparable to the estimated sodium coprecipitation loss (about 5 mg/g dry filter cake). Sodium sulfite, bisulfite, and sulfate were added at a rate equivalent to the loss of liquor by entrainment in discarded filter cake and in the ratio at which these components were present in the liquor. The feed rate of each sulfur species was adjusted daily according to the results of liquor analyses so that the total sodium salts lost were replenished by adding simulated scrubbing liquor. Scrubber performance is discussed below with emphasis on the period of steady-state operation.

(1) Sulfur dioxide absorption: During Phase 2, over 86 percent $SO_2$ removal efficiency was achieved. The cause for this slight drop in removal efficiency, relative to Phase 1, was undetermined; however, slight changes in scrubber operating parameters would probably have restored the removal efficiency to the 90-plus percent level.

(2) System chemistry: The most obvious change was the accumulation of sulfate ion in the scrubbing liquor as shown in Figure 3. The steady-state sulfate concentration reached 0.9 gmole/ℓ. This was up from the 0.44 gmole/ℓ level experienced during the high sodium consumption operation. The pH of scrubbing liquor dropped by about 0.2 in both the regenerated liquor and the spent absorbent solution after steady state was reached. Laboratory experiments were performed to measure the pH of synthetic scrubbing liquor of similar compositions. Figure 4 indicates that a 0.1 to 0.2 pH drop was obtained by spiking the solution with sodium sulfate. It appears that sulfate accumulation contributed to the pH drop and thus may also have reduced the $SO_2$ removal with all other factors held constant.

(3) Limestone addition: Limestone utilization greater than 90 percent was constantly attained despite the accumulation of sulfate. The data confirmed that limestone dissolved adequately in the multiple reactor system and limestone utilization should not be a concern with the limestone-regenerated dual alkali process.

(4) Sodium makeup: Soda ash consumption rate was maintained at 0.016 mole $Na_2CO_3$/mole $SO_2$ absorbed in order to simulate the zero liquor loss assumption and represents the minimum soda ash requirement. All other actual sodium losses were made up with $Na_2SO_4$, $Na_2SO_3$, and $NaHSO_3$ in the ratio found daily in the regenerated liquor.

(5) Regeneration: Most of the scrubbing liquor regeneration reaction occurred in the first two reactors, as observed previously during high sodium consumption operation. However, the settling rate of the slurry in the last reactor decreased with the accumulation of sulfate ion. Figure 5 indicates a general trend of lower settling rates with increasing sulfate-to-sulfite ratios.

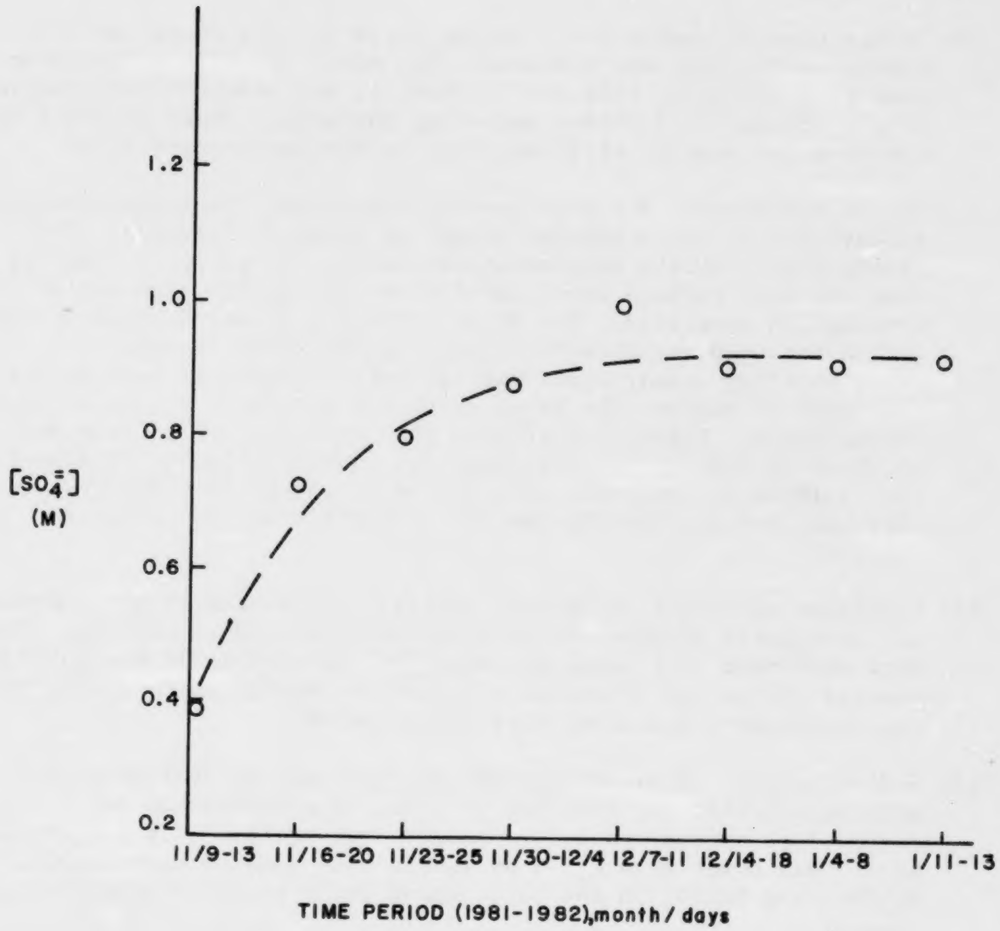


Figure 3. Sulfate accumulation in scrubbing liquor at the EPA/IERL-RTP 0.1 MW dual alkali pilot plant.

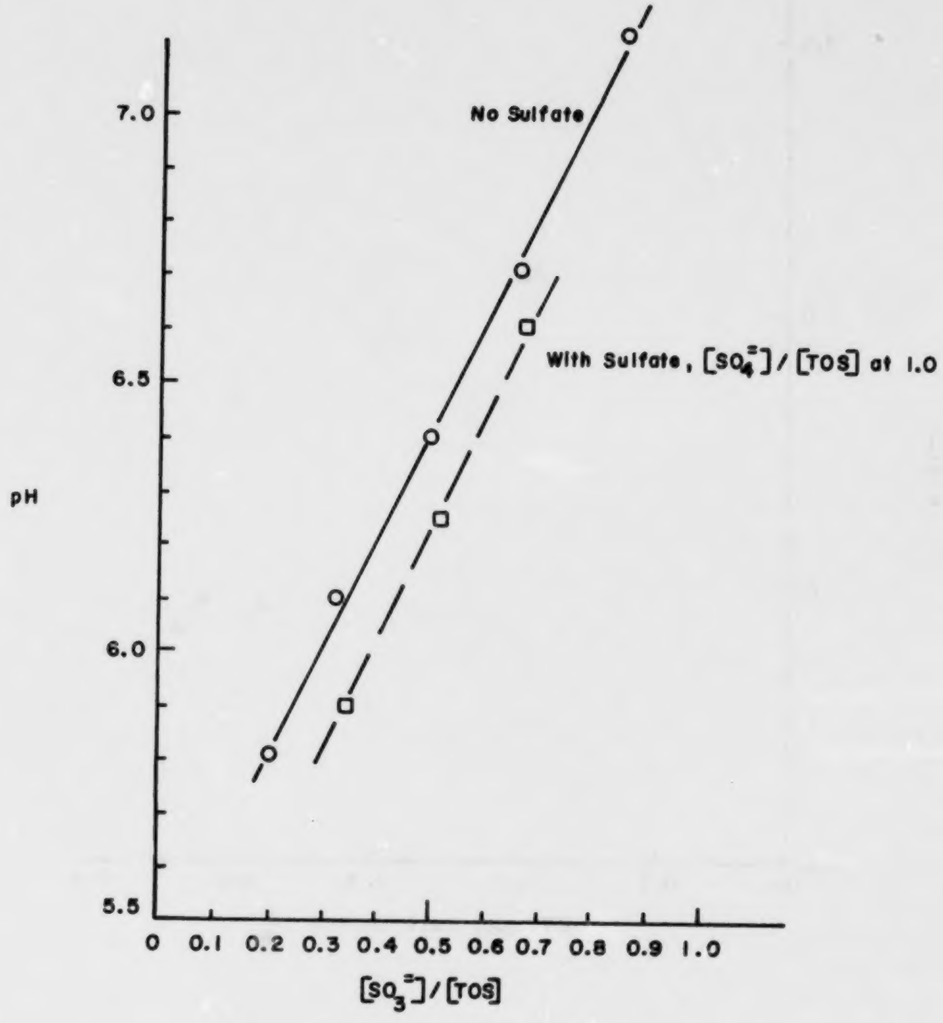


Figure 4. Effect of sulfate on pH of synthetic dual alkali scrubbing liquor.

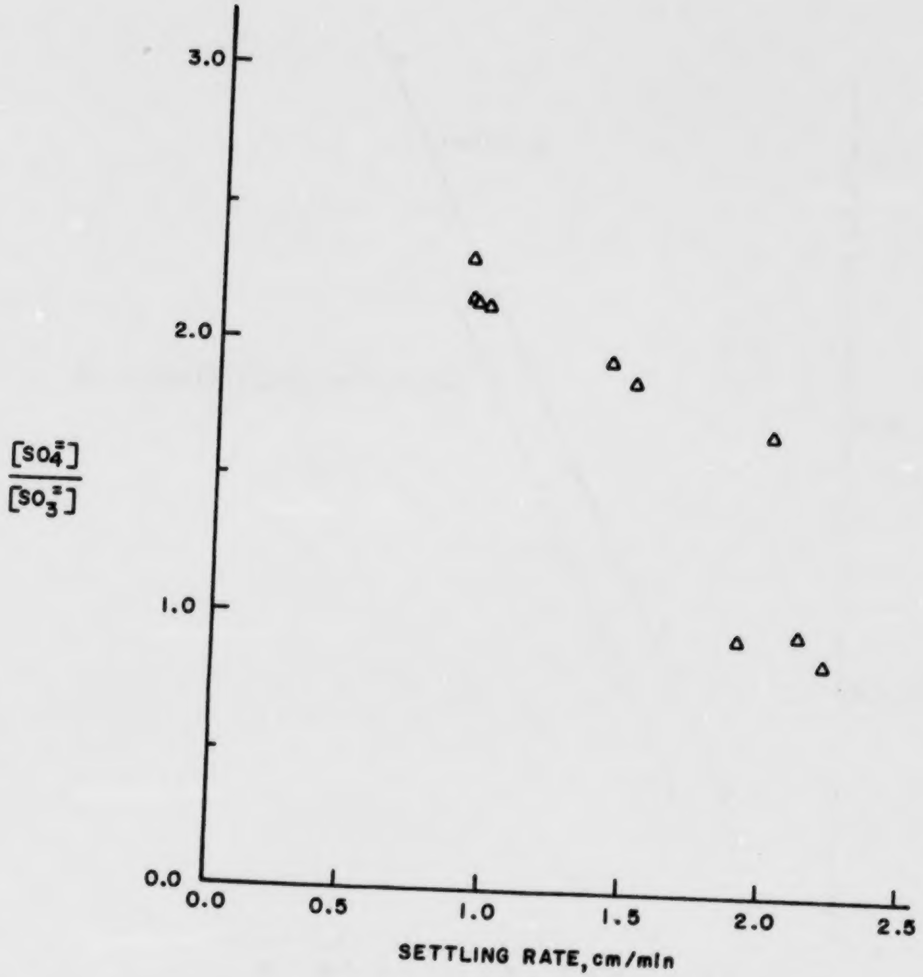


Figure 5. Reactor slurry settling rate as a function of sulfate-to-sulfite ratio in the EPA/IERL 0.1 MW dual alkali pilot plant.

(6) Filter cake quality: Two changes in filter cake quality were observed: the percent of solids and the sulfate content. Figure 6 shows that the filter cake percent of solids dropped with the accumulation of sulfate ion. At steady state, the filter cake contained 45 to 50 percent solids which represents an improvement over the 40 to 45 percent obtained before modification of the reactor system. Data in the literature indicate that the sulfate coprecipitation rate in the filter cake is proportional to the sulfate-to-sulfite ratio in the scrubbing liquor(5). Liquor analysis indicated that the sulfate-to-sulfite ratio increased from 0.9 to 2.0 during the transition from Phase 1 to Phase 2 operation. Solids analysis indicated a corresponding increase in filter cake sulfate content. A comparison of pilot plant data with the correlation developed by A. D. Little(5) is shown in Figure 7.

## Significance of the Results

(1) The high sodium (Phase 1) and low sodium (Phase 2) consumption operating conditions represented two extreme cases of system operation. The system operability and technical feasibility of the limestone DA process was thus demonstrated by pilot plant testing at both extremes relative to system liquor loss. The actual operating conditions of full-scale limestone DA scrubbers are likely to be between the two cases studied.

(2) The high $SO_2$ removal efficiency and limestone utilization achieved by pilot plant tests confirmed previous pilot plant and prototype data. Equivalent scrubber performance with lime and limestone is expected with full-scale systems, as was observed at Scholz.

(3) Soda ash consumption rate was considerably reduced. Soda ash could be a substantial operating cost for the limestone DA process as shown by economic analysis in the next section. The reduction of soda ash makeup rate from 0.29 moles $Na_2CO_3$/mole $SO_2$ removed (Scholz) to 0.13 moles $Na_2CO_3$/mole $SO_2$ removed (this work) could be translated into significant saving in annual operating cost. The low soda ash consumption rate demonstrated by pilot plant simulation tests (0.016 moles $Na_2CO_3$/mole $SO_2$ removed) makes the economics of limestone DA very attractive relative to lime DA. Good crystallization in the limestone DA process, which can be enhanced with certain reactor system designs, may also result in a significant reduction in sodium consumption.

(4) Significant improvement in filter cake quality was accomplished. Filter cake with solids as high as 75 to 80 percent was produced during Phase 1. The sulfate concentration in the scrubbing liquor and reactor design were identified as important factors in determining the solids quality.

## COMPARISON OF LIME AND LIMESTONE DUAL ALKALI PROCESSES

Both technical and economical comparisons were made between lime and limestone regenerated dual alkali processes. The data used for comparisons were all obtained from the IERL-RTP pilot plant with the same (tray column) scrubber. Table 2 lists the average scrubber performance obtained from pilot

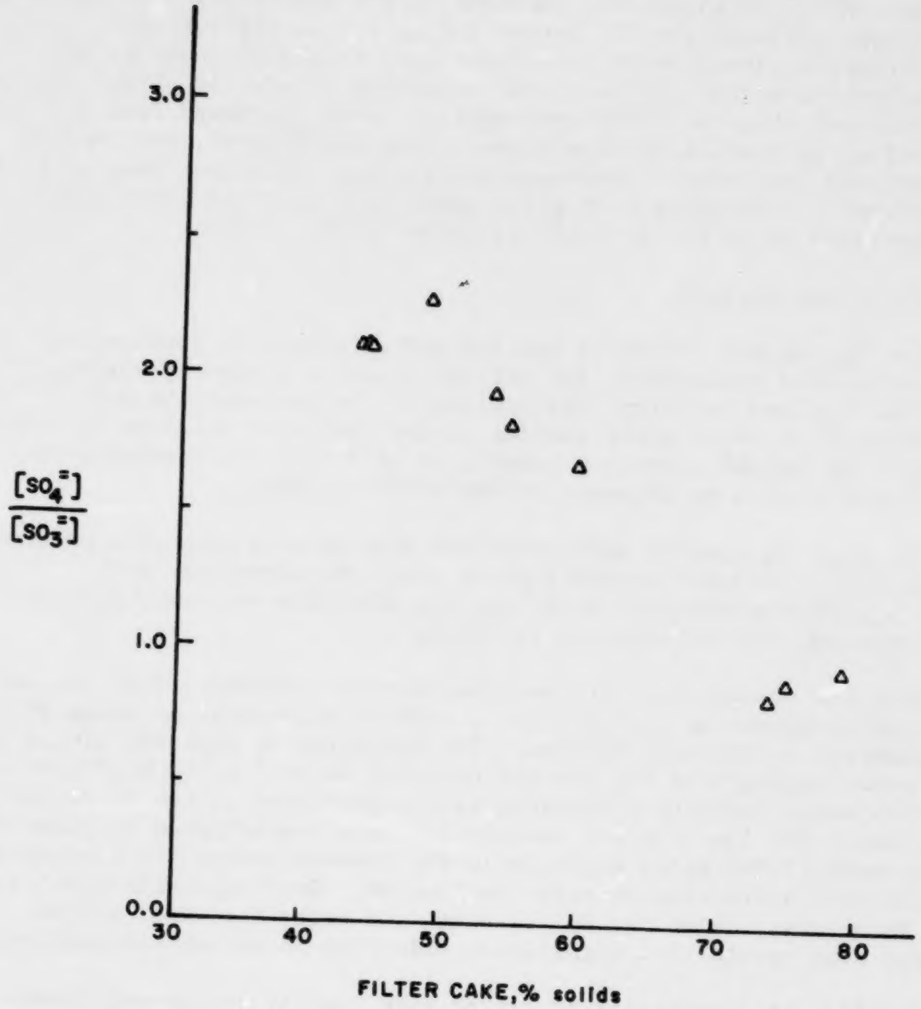


Figure 6. Filter cake percent of solids as a function of sulfate-to-sulfite ratio at the EPA/IERL 0.1 MW dual alkali pilot plant.

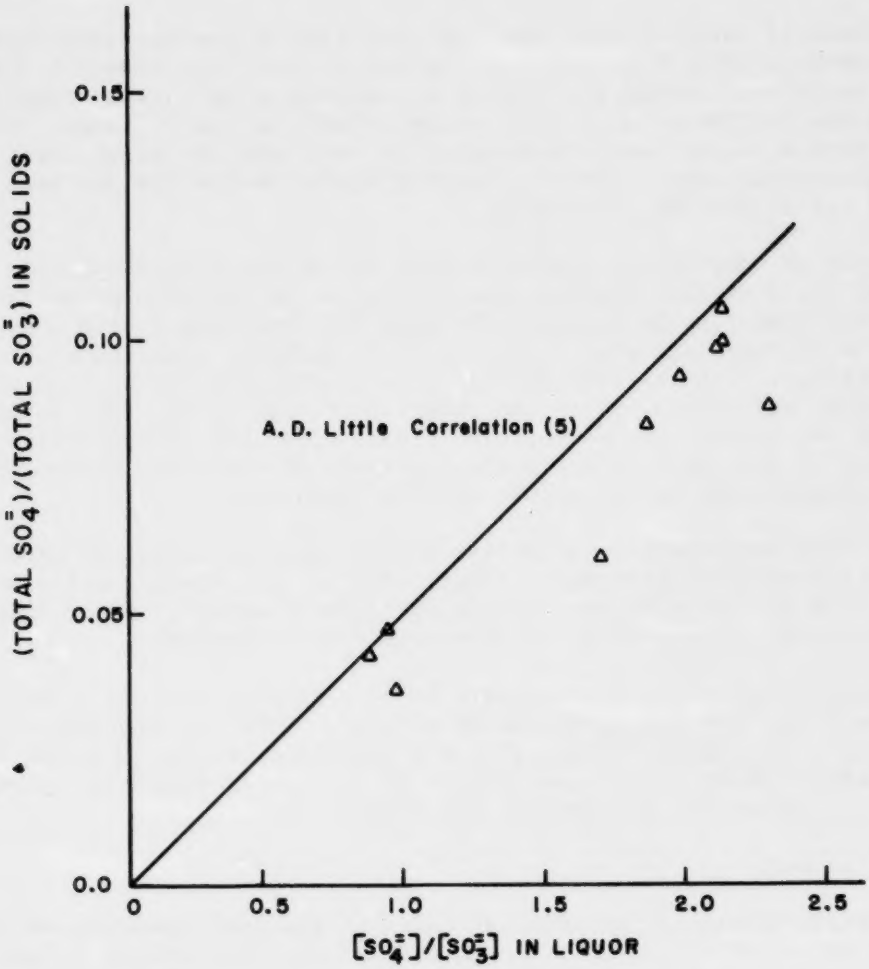


Figure 7. Ratio of total sulfate to total sulfite in reactor effluent solids as a function of sulfate-to-sulfite ratio in regenerated liquor at the EPA/IERL 0.1 MW dual alkali pilot plant.

plant lime and limestone dual alkali tests. Comparing the lime data with commercial scrubber performance indicates that the IERL-RTP pilot plant simulated the full-scale operation closely and that the pilot scrubber performance reflects actual operating conditions(7,8).

## TECHNICAL ANALYSIS

As shown in Table 2, both lime and limestone DA demonstrated high $SO_2$ removal (greater than 90 percent) at low L/G ratios (less than 1.4 $\ell/m^3$). No scrubber recycle is needed for limestone regenerated DA systems since calcium carbonate scaling is not a concern at the relatively low pH range. More reactors with a longer total residence time were used for pilot plant limestone regeneration runs. However, reactor system design has not been optimized for full-scale application.

Whereas pH control was used with lime DA, stoichiometry control (adjusting the limestone feed rate according to the $SO_2$ absorption rate) was employed for limestone DA testing. Because the limestone system operates in a very narrow pH range and with a high reactor residence time, pH control may not be suitable. Considerably higher active sodium and TOS concentrations were required and maintained in the limestone DA system in order to achieve acceptable operation. Due to the high dissolved solids concentration, a tight liquor loop is more desirable for the limestone DA than the lime DA system to minimize reagent consumption resulting from liquor loss.

Both lime and limestone processes demonstrated satisfactory (greater than 90 percent) reagent utilization. Filter cake of equivalent quality was expected from oxidation rates. During the shorter duration pilot lime DA operation, up to 60 percent waste cake solids were obtained.

Soda ash consumption rate appears to be a strong function of oxidation rate in both the lime and limestone DA systems. Soda ash consumption rate will probably be slightly higher with the limestone DA than with the lime DA process under similar conditions, due to the generally higher dissolved sodium compound concentrations required in the former.

### Economic Analysis

Table 3 shows the major chemical costs of lime and limestone DA processes estimated for a 500 MW FGD unit. High sulfur coal (3.5 percent sulfur content) was assumed with 90 percent of the sulfur evolved as $SO_2$ in the untreated flue gas. $SO_2$ removal efficiency of 90 percent was assumed. The lime, limestone, and soda ash consumption rates were based on test results generated by the IERL-RTP pilot plant and verified to some extent by full-scale test results or prototype results at Louisville Gas & Electric and Gulf Power, respectively.

Table 3 indicates that more than $1 million savings in chemical cost could be realized per year by converting from a lime to a limestone DA process. The relative prices of lime and limestone might affect the economic scenerio, but the relative price of lime to limestone is likely to increase due to the rise of energy cost, and thus limestone DA would be favored. Since

## TABLE 2. COMPARISON OF SYSTEM PERFORMANCE BETWEEN LIME AND LIMESTONE DUAL ALKALI PROCESSES

| | Limestone | | Lime |
|---|---|---|---|
| | High sodium consumption | Low sodium consumption | Normal |
| System Performance | | | |
| $SO_2$ removal, % | 90-92 | 86-90 | 90-92 |
| Lime/limestone consumption, moles/mole $SO_2$ absorbed | 0.9-1.0 | 1.0-1.1 | 0.9-1.0 |
| Soda ash consumption, mole/mole $SO_2$ absorbed | 0.13 | 0.016 | 0.05 |
| Waste quality, % solids | 70-75 | 45-50 | 50-55 |
| Absorber | | | |
| L/G, $\ell/m^3$ | 0.40-0.54 | 0.40-0.54 | 0.80-1.08 |
| $\Delta P$, cm $H_2O$ | 15-18 | 15-18 | 15-18 |
| Recycle | No | No | Yes |
| Reactor System | | | |
| No. of tanks | 3 | 3 | 2 |
| Residence time, min | 90 | 90 | 45 |
| Solids settling rate, cm/min | 1.5-2.0 | 0.9-1.0 | - |
| Process Chemistry | | | |
| Regenerated liquor pH | 6.6 | 6.4 | 12 |
| Spent absorbent pH | 6.1 | 5.8 | 5.9 |
| Active Na, mole/ℓ | 1.35 | 1.35 | 0.44 |
| TOS in regenerated liquor, mole/ℓ | 0.87 | 0.88 | 0.22 |
| Process control | Stoichiometry | Stoichiometry | pH |
| Lime/limestone utilization by waste analysis, % | 90-95 | 90-95 | 93-104* |

*104% utilization results from additive effects attributable to combination of several pieces of analytical data each of which has a given associated error band.

## TABLE 3. COMPARISON OF CHEMICAL COSTS BETWEEN LIME AND LIMESTONE DUAL ALKALI PROCESSES

| | Limestone | | Lime |
|---|---|---|---|
| | High sodium consumption $1 M/yr | Low sodium consumption $1 M/yr | Normal $1 M/yr |
| Limestone | 1.74 | 1.96 | – |
| Lime | – | – | 4.0 |
| Soda ash | 1.98 | 0.3 | 0.76 |
| Total | 3.72 | 2.26 | 4.76 |

Assumptions:

| | |
|---|---|
| • Power plant | 500 MW<br>7200 hr operation/year |
| • Coal properties | 3.5% sulfur, 25.6 MJ/kg (11,000 Btu/lb)<br>170.1 m ton (187.5 ton) coal burned/hour<br>90% of sulfur in coal evolves as $SO_2$<br>90% $SO_2$ removal from flue gas |
| • Cost | Limestone @ \$13.61/m ton (\$15/ton)<br>Lime @ \$54.43/m ton (\$60/ton)<br>Soda ash @ \$108.86/m ton (\$120/ton) |
| • Consumption rate | Lime DA; 1.0 mole lime and 0.05 mole soda ash per mole of $SO_2$ absorbed<br>Limestone, high sodium consumption; 0.97 mole limestone and 0.13 mole soda ash per mole of $SO_2$ absorbed<br>Limestone, low sodium consumption; 1.09 mole limestone and 0.02 mole soda ash per mole of $SO_2$ absorbed |

the technical analysis indicated no major differences between lime and limestone DA equipment, it is concluded that economic benefit can be derived by converting from lime to limestone in DA systems with minimal increase in capital cost for greater reactor cost. Limestone grinding equipment cost would probably be offset by saving in lime slaking equipment cost.

## CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are drawn from this work:

(1) The limestone DA process is a technically feasible FGD system. Pilot plant tests confirmed that over 90 percent $SO_2$ removal at L/G ratios of 0.40-0.54 $\ell/m^3$ (3-10 gal./1000 cfm) is achievable.

(2) Economic benefits can be realized by converting from lime to limestone DA. More than $1 million per year in operating cost may be saved by using limestone instead of lime in a 500 MW FGD unit.

(3) A relatively high concentration of TOS (0.85 M suggested) may be required in the limestone DA scrubbing liquor to provide adequate absorption capacity and to avoid producing non-settling solids.

(4) Crystallization is an important parameter affecting the operability of limestone DA processes. More research is suggested to optimize the reactor system design and, therefore, further enhance system reliability and reduce the soda ash consumption rate.

(5) High oxidation results in increased consumption due to:

(a) Conversion of $Na_2SO_3$ to $Na_2SO_4$ and the resultant loss of $Na_2SO_4$
(b) Additional losses of liquor associated with poor quality filter cake
(c) The loss of liquor containing a higher dissolved solids concentration.

Measures minimizing oxidation level and sulfate accumulation should therefore be considered in full-scale design and operation to ensure high quality filter cake.

(6) Due to the sulfate accumulation effect and to the inability to wash the waste cake completely free of sodium compounds, zero sodium consumption operation is economically favorable but not technically possible. Optimum operating conditions will be determined by engineering trade-offs and site-specific requirements.

# REFERENCES

1. Smith, M. P., M. T. Melia, B. A. Laseke, Jr., and N. Kaplan, "Recent Trends in Utility Flue Gas Desulfurization," in Proceedings: Symposium on Flue Gas Desulfurization - Houston, Texas, October 1980, Volume 1, EPA-600/9-81-019a (NTIS PB81-243156), April 1981.

2. Kaplan, N., "Summary of Utility Dual Alkali Systems," in Proceedings: Symposium on Flue Gas Desulfurization - Las Vegas, Nevada, March 1979, Volume II, EPA-600/7-79-167b (NTIS PB80-133176), July 1979.

3. LaMantia, C. R., R. R. Lunt, J. E. Oberholtzer, E. L. Field, and J. R. Valentine, "Final Report: Dual Alkali Test and Evaluation Program, Volume II. Laboratory and Pilot Plant Programs," EPA-600/7-77-050b (NTIS PB272-770), May 1977.

4. Oberholtzer, J. E., L. N. Davidson, R. R. Lunt, and S. P. Spellenberg, "Laboratory Study of Limestone Regeneration in Dual Alkali Systems," EPA-600/7-77-074 (NTIS PB272-111), July 1977.

5. Valencia, J. A., J. F. Peirson, Jr., and G. J. Ramans, "Evaluation of the Limestone Dual Alkali Prototype System at Plant Scholz - Final Report," EPA-600/7-81-141b (NTIS PB82-110685), August 1981.

6. Chang, C. S., and G. T. Rochelle, "$SO_2$ Absorption into NaOH and $Na_2SO_3$ Aqueous Solutions," AIChE 88th National Meeting, Philadelphia, PA, June 8-12, 1980.

7. Durkin, T. H., J. A. Van Meter and L. K. Legatski, "Operating Experience with the FMC Double Alkali Process," in Proceedings: Symposium on Flue Gas Desulfurization - Houston, Texas, October 1980, Volume 1, EPA-600/9-81-019a (NTIS PB81-243156), April 1981.

8. Van Ness, R. P., N. Kaplan, and D. A. Watson, "Dual Alkali Demonstration Project Interim Report," Ibid.

# ACKNOWLEDGEMENT

This work was funded in part by Peabody Process Systems.

The authors wish to express their sincere gratitude to J. David Mobley, Robert H. Borgwardt and Michael A. Maxwell of EPA/IERL-RTP for their involvement in the review and planning of this work. The effort and support of Acurex's RTP pilot plant staff is greatly appreciated.

## Session 4: SPECIAL STUDIES

Dorothy A. Stewart, Chairman
Electric Power Research Institute
Palo Alto, CA

# CHLORIDE ION EFFECTS
# ON
# LIMESTONE FGD SYSTEM PERFORMANCE

By

John C. S. Chang
Acurex Corporation
P. O. Box 13109
Research Triangle Park, North Carolina 27709

and

Dennis Laslo
Peabody Process Systems, Inc.
835 Hope Street
Stamford, Connecticut 06907

For presentation at:
EPA/EPRI FGD Symposium
Hollywood, Florida
May 18, 1982

## ABSTRACT

The effects of high concentrations of chloride ions on limestone flue gas desulfurization were studied in a 0.1 MW pilot plant. Significant changes in the pilot plant pH, $SO_2$ removal efficiency, solids settling rate and the gypsum saturation level were observed as the calcium chloride concentration increased. The same effects were not as dramatic when operating in a forced oxidation mode. A discussion of the test data is presented.

# ACKNOWLEDGEMENTS

The authors wish to express sincere gratitude to the following individuals for their continued support and assistance throughout the test program.

David Mobley - Environmental Protection Agency

Robert Borgwardt - Environmental Protection Agency

Norman Kaplan - Environmental Protection Agency

Mike Maxwell - Environmental Protection Agency

Gary Rochelle - University of Texas

Gerald Janik - New York State Electric and Gas

Steve DeMarco - New York State Electric and Gas

Even Bakke - Peabody Process Systems, Inc.

Herb Dempsey - Acurex Corporation

Professor Rochelle was retained as a technical consultant for portions of this project.

Mr. David Mobley was the EPA project officer.

## INTRODUCTION

The advent of tightly closed water loops in lime/limestone desulfurization systems, combined with the combustion of high chloride coals and the use of cooling tower blowdown as makeup water has produced a situation where high concentrations of soluble chlorides in the absorbing liquor should be considered as a design factor.

The two primary sources of the chloride ion in FGD liquor are the chloride in the coal and makeup water, especially if cooling tower blowdown is utilized. Small amounts of chlorides may be present in the limestone and flyash. Upon combustion of the coal, most chlorides will exist as gaseous HCl. The solid phase chlorides, detectable in boiler bottom ash and electrostatic precipitator ash (probably due to salt precipitation or sorption of HCl on alkaline flyash) are very low in concentration(1). Absorption of HCl in the FGD scrubber liquor will result in the corresponding increase in the concentration of calcium and chloride ions as shown below, using limestone as the alkali.

$$HCl_{(g)} + H_2O \longrightarrow H^+ + Cl^- + H_2O$$

$$CaCO_{3(s)} + 2H^+ \longrightarrow Ca^{2+} + CO_2 + H_2O$$

However, predicting the quantity of HCl reaching the absorber is difficult since little data are available. PEDCo monitored chloride concentrations at R. D. Morrow Station and determined roughly by calculated mass balance that 95% of the chlorides in the coal reached the absorber as HCl and 95% of the HCl was absorbed in the FGD liquor although all process streams were not measured for chlorides(2).

In order to broaden this data base, a survey of 32 utilities which own or operate 60 FGD systems characterized as having closed water loops was performed by PEDCo for Peabody Process Systems(3). Detailed data on chlorides were obtained for only three systems and general chloride data were obtained for another 15 systems. For the three systems where detailed chloride data were reported, chloride concentrations of 1500 ppm* (Pleasants 1 and 2; 0.04% Cl Coal), 11,000 ppm (R.D. Morrow 1 and 2; 0.11% Cl Coal), and 4200 ppm (Dallman 3; 0.11% Cl Coal) were reported. The investigation indicated little or no data exist for ash and reagent chloride analysis.

The station with the highest reported chloride concentration, R. D. Morrow, has indicated that switching from calcitic to high magnesium limestone alleviated scaling problems (assumed to be caused by the chlorides) by providing high levels of dissolved magnesium in the absorbing liquor.

The second primary source of chloride accumulation in FGD systems, makeup water, is also a source of sodium, magnesium, and other cations. Thus, chloride accumulation from makeup water is likely to have different effects on FGD chemistry than accumulation from HCl gas absorption.

---

*One ppm is equivalent to one mg/l.

The effects of chlorides on limestone desulfurization system performance have previously been studied, primarily in the range of less than 30,000 ppm, but the results are mixed:

> Bechtel(4) first reported that increased chloride concentrations increased $SO_2$ removal efficiency at a constant hold tank pH in the Shawnee spray tower and Turbulent Contact Absorber (TCA) with chloride concentrations approaching 20,000 ppm. Later, Bechtel's final analysis of the data(5) indicated a slight increase in $SO_2$ removal efficiency only on the spray tower when using lime as an alkali. Chlorides had no significant effects on $SO_2$ removal efficiencies in the TCA with either alkali.
>
> Borgwardt(6) found a decrease in the rate of limestone dissolution at 5000 and 20,000 ppm $CaCl_2$ (as $Cl^-$) in beaker titrations. Nitrogen sparging significantly improved the dissolution rate presumably by stripping $CO_2$ gas from solution.
>
> Borgwardt(6) also found deteriorative results due to the chlorides in EPA's IERL/RTP pilot plant using the 9" diameter TCA injected with HCl gas. Little change in absorber performance was noted in tests with natural oxidation at 5000 ppm $Cl^-$ and forced oxidation tests at 22,000 ppm $Cl^-$; however, when chlorides were increased from 0 to 19,000 ppm in the natural oxidation mode, $SO_2$ removal efficiency dropped from 86% to 74% and the recycle tank pH decreased from 6.0 to 5.4.
>
> Rochelle(7) measured decreased limestone dissolution using a pH-stat at high concentrations of $CaCl_2$, NaCl, and $MgCl_2$ at a pH of 5.0 with nitrogen sparging. He attributed this effect to slowed $H^+$ diffusivity in high ionic strength solutions. Results indicated that increasing $CaCl_2$ concentrations from 0.1M to 2.0M decreased the limestone rate of dissolution from $1.9 \times 10^{-9}$ cm$^2$/sec to $2.94 \times 10^{-10}$ cm$^2$/sec.
>
> Rader, et al(8,9) reported a slight increase in $SO_2$ removal efficiency in a pilot spray tower at constant limestone stoichiometry and chloride concentrations as high as 25,000 ppm. Also reported was an increase in gypsum scaling potential as the chloride concentration increased.
>
> Kobe Steel(10) indicated $SO_2$ removal efficiency increases with chloride concentrations as high as 30 weight percent using lime in a unique clear solution $CaCl_2$ process.
>
> Borgwardt(11) also studied chloride accumulation in limestone FGD scrubbers using HCl gas and simulated cooling tower blowdown ($Na_2SO_4$ in water saturated with gypsum) as system makeup water in EPA's pilot plant. An improvement in $SO_2$ removal efficiency was noted at chloride levels of 23,000 ppm and sodium levels of 12,000 ppm over the fresh waster makeup base case (17,000 ppm $Cl^-$, and no $Na^+$). Borgwardt attributed the improvement to favorable ion diffusivities and equilibrium constant. Scaling in the absorber was consistently observed at sodium levels exceeding 15,000 ppm and an $SO_2$ make-per-pass exceeding 8.0 mM.

Chlorides are also a source of concern for alloy corrosion but this paper will deal exclusively with its effects on FGD chemistry. A comprehensive literature search(12) and experiments(13) in the corrosion area have been performed and will be published shortly by the Electric Power Research Institute (EPRI).

The current study was initiated in order to broaden the data base of chloride effects on limestone FGD system chemistry, especially at concentrations exceeding 20,000 ppm. Test work was performed at the Environmental Protection Agency's 0.1 MW Pilot Plant by Acurex Corporation. Under a cooperative agreement, EPA-IERL/RTP supported the test program by contributing the equipment, facilities and the time of its staff. Major funding for the project was by Peabody Process Systems, Inc., Stamford, CT and by New York State Electric and Gas of Binghamton, N.Y.

## THEORETICAL ANALYSIS

When HCl in flue gas is absorbed by limestone slurry and accumulates in the scrubbing liquor as $Cl^-$, the liquid phase $Ca^{2+}$ concentration increases correspondingly to maintain ionic balance in the absence of other cations. At a constant limestone stoichiometric ratio, defined as moles of limestone added per mole of $SO_2$ absorbed, increasing the calcium ion concentration affects the system chemistry and scrubber performance significantly. As the literature survey indicated, higher calcium ion concentrations have resulted in lower equilibrium pH and increased gypsum scaling potential.

### EQUILIBRIUM pH:

The equilibrium $Ca^{2+}$ concentration is related to the $CO_3^{2-}$ concentration by the solubility product equation(5)

$$A_{Ca^{2+}} \cdot A_{CO_3^{2-}} = K_{CaCO_3} = \text{Constant} \qquad (1)$$

The $CO_3^{=}$ concentration, in turn, is related to the $H^+$ concentration (at constant $CO_2$ partial pressures):

$$A^2_{H^+} \cdot A_{CO_3^{2-}} = K_{H_2CO_3} \cdot P_{CO_2} = \text{Constant} \qquad (2)$$

Thus, as the $Ca^{2+}$ concentration increases, the $CO_3^{2-}$ concentration decreases to maintain a constant equilibrium product as shown in Equation (1). The $H^+$ concentration must then increase (or alternately, the pH must decrease) in accordance with Equation (2).

Under natural oxidation conditions, $P_{CO_2}$ of the limestone scrubbing liquor is partially limited by the flue gas $CO_2$ concentration and can be assumed to be relatively constant. Therefore, even a finite approach to equilibrium will require a pH drop at higher $Ca^{2+}$.

However, under in-loop forced oxidation conditions, equilibrium pH can not be directly related to $Ca^{2+}$ by Equations (1) and (2) since oxidizer air not only oxidizes dissolved $SO_2$ but also strips off carbon dioxide which makes $P_{CO_2}$ and the system pH primarily a function of the sparger air rate.

Therefore, less of an effect of calcium chloride on equilibrium pH is expected with forced oxidation.

## $SO_2$ ABSORPTION

The absorption of $SO_2$ from flue gas by limestone slurry can be regarded as gas absorption accompanied by chemical reactions in the liquid phase. Since the $SO_2$ absorption rate is primarily controlled by liquid phase mass transfer resistance(14) and the gas phase $SO_2$ diffusion rate will be unaffected by the presence of dilute HCl gas, the major effect of chloride ions on the $SO_2$ mass transfer rate is expected to occur in the liquid phase.

The liquid side mass transfer rate of $SO_2$ across the gas-liquid interphase can be expressed as a molar flux:

$$N = \phi\ k_L\ (C^{i}_{SO_2} - C^{\circ}_{SO_2}) \tag{3}$$

The mass transfer enhancement factor, $\phi$, is a function of the liquid phase chemical reactions. The liquid phase mass transfer coefficient, $k_L$, is related to the diffusion rate and the liquid phase $SO_2$ concentration, $C_{SO_2}$, is to the solubility of sulfur dioxide. As will be shown, each of these parameters is affected by the increase of chloride ion concentrations.

The concentration of sulfur dioxide at the gas-liquid interface, $C^{i}_{SO_2}$, can be related to the partial pressure of $SO_2$ at the interface, $P^{i}_{SO_2}$, by an expression similar to Henry's Law:

$$\alpha \cdot P^{i}_{SO_2} = C^{i}_{SO_2} \quad . \tag{4}$$

The correlation constant, $\alpha$, is a function of liquid phase ionic strength, I, which increases with the accumulation of chloride ion:

$$\log\frac{\alpha}{\alpha_w} = k\ I\ , \qquad \text{with } k = 0.019 \text{ for } CaCl_2{}^{(15)} \tag{5}$$

and

$$I = \frac{\Sigma\, n_j^2 C_j}{2} \tag{6}$$

According to the penetration theory, the liquid phase mass transfer coefficient, $k_L$, is proportional to the square root of the sulfur dioxide diffusivity, D. Accumulation of calcium chloride affects the diffusivity (thus $k_L$) through the change of liquid viscosity:(16)

$$\log \frac{D}{D_w} = -0.637 \log (1 + 0.2775\ C_{CaCl_2}) \tag{7}$$

Equations (5) and (7) indicate that the increase of chloride ion concentration enhances the solubility but decreases the diffusivity of dissolved sulfur dioxide. In terms of the $SO_2$ mass transfer rate, Equation (3), these two factors tend to offset each other and a minimal effect due to diffusivity and solubility change on $SO_2$ absorption rate is expected. Calculations indicate that an increase of chloride concentration from 200 ppm to 100,000 ppm only changes the product of $k_L$ and $C^i_{SO_2}$ by +8 percent.

However, the mass transfer enhancement factor,  , can change significantly when calcium chloride accumulates. This can best be explained by examining the various reactions which occur in solution. First, the hydrolysis reaction is expected to occur when $SO_2$ is dissolved in water:(17)

$$SO_2 + H_2O \longrightarrow H^+ + HSO_3^- \tag{8}$$

In addition, alkaline species derived from dissolved limestone react with sulfur dioxide to form bisulfite ions. More than ten chemical reactions involving dissolved $SO_2$ and alkalinities have been identified by Hatfield and Slack.(18) In limestone scrubbers, the most important are:

$$SO_2 + SO_3^{2-} + H_2O \longrightarrow 2HSO_3^- \tag{9}$$

$$SO_2 + CaSO_3 + H_2O \longrightarrow 2HSO_3^- + Ca^{2+} \tag{10}$$

$$SO_2 + HCO_3^- \longrightarrow HSO_3^- + CO_2 \tag{11}$$

$$SO_2 + CaHCO_3^+ \longrightarrow HSO_3^- + Ca^{2+} + CO_2 \tag{12}$$

Under natural oxidation conditions, the hydrolysis reaction is depressed by the relatively high bisulfite concentration and the mass transfer enhancement,  , is dominated by reactions (9) to (12).

Rochelle and King(14) suggested that  is related to total alkalinity as

$$= 1 + \frac{D_A}{D} \frac{C_A}{C^i_{SO_2}} \tag{13}$$

If we define the alkalinity concentration, $C_A$, as the total concentration of $SO_3^{2-}$, $CaSO_3$, $HCO_3^-$, and $CaHCO_3^+$; the chloride ion effect on $C_A$ can be estimated by the Bechtel Modified Radian equilibrium computer program.(19) Table 1 lists the calculated concentrations of each alkaline species and the estimated total alkalinity at various chloride levels. It is evident that the total alkalinity is reduced by more than 40 percent with the accumulation of chloride ions from 200 ppm to

20,000 ppm. With the assumption that $D_A/D$ equals 1 and $C^{\circ}_{SO_2}$ is negligible compared with $C^{i}_{SO_2}$, the relative liquid side mass transfer resistance, $\frac{1}{\phi k_L \alpha}$, at various chloride ion concentrations, can be estimated by Equations (5), (7) and (13) at a given interfacial $SO_2$ partial pressure. Figure 1 indicates that the liquid side mass transfer resistance increases by more than 50 percent when the chloride concentration increases from 200 ppm to 20,000 ppm at 1000 ppm $P^{i}_{SO_2}$. Since the $SO_2$ absorption rate is primarily controlled by liquid phase mass transfer resistance, a corresponding drop in $SO_2$ removal efficiency is expected with the accumulation of chloride ions in the scrubbing liquor.

As shown in Table 1 and Figure 1, the decrease of total alkalinity or, the increase of mass transfer resistance, beyond 20,000 ppm $Cl^-$ is not as significant as below 20,000 ppm $Cl^-$. However, the trend indicates that the $SO_2$ removal efficiency should continue to drop with further increase of chloride ion concentration beyond 20,000 ppm.

Under in-loop forced oxidation conditions, less of an effect on the $SO_2$ removal efficiency is expected due to chloride ions since the $SO_2$ hydrolysis reaction, which is not affected by chloride ions, plays a very important role in liquid phase mass transfer(20).

## GYPSUM SCALE

Calcium chloride accumulation has two major impacts on gypsum scaling potential in a limestone scrubber: (1) transformation of the scrubber operation from a subsaturation to a supersaturation mode with respect to calcium sulfate, and (2) causing a substantial increase in relative saturation of gypsum across the scrubber.

In order to minimize the scaling potential, a limestone scrubber is preferentially operated at a subsaturated mode with respect to gypsum, or:

$$\text{R.S. (Relative Saturation)} = \frac{A_{Ca^{2+}} \cdot A_{SO_4^{2-}}}{K_{sp}} < 1.0 \qquad (14)$$

To maintain the subsaturation mode, all sulfate resulting from oxidation in the scrubber must coprecipitate with calcium sulfite to form a "solid solution". The coprecipitation mechanism is equilibrium controlled and has been empirically correlated(21), yielding the relationship:

$$\left(\frac{SO_4}{SO_3}\right)_{solid} = K' A^{x}_{Ca^{2+}} \cdot A^{y}_{SO_4^{2-}} \qquad (15)$$

where y > x

TABLE 1. CALCULATED EFFECT OF $CaCl_2$ ACCUMULATION ON TOTAL DISSOLVED ALKALINITY

|  |  | Dissolved Alkalinity (mM) |  |  |
|---|---|---|---|---|
| Ion | Base Case* | Chloride Concentration (ppm x $10^{-3}$) 20 | 50 | 100 |
| $HCO_3^-$ | 2.73 | 0.705 | 0.422 | 0.212 |
| $CaHCO_3^+$ | 0.152 | 0.789 | 1.03 | 1.12 |
| $SO_3^{2-}$ | 0.218 | 0.024 | 0.01 | - |
| $CaSO_3$ | 0.744 | 0.646 | 0.52 | 0.363 |
| Total | 3.84 | 2.16 | 1.98 | 1.69 |

*Assume: $CaCO_3$ saturation = 0.25

$CaSO_3$ saturation = 1.5

pH = 6.0

$Ca^{2+}$ = 250 ppm

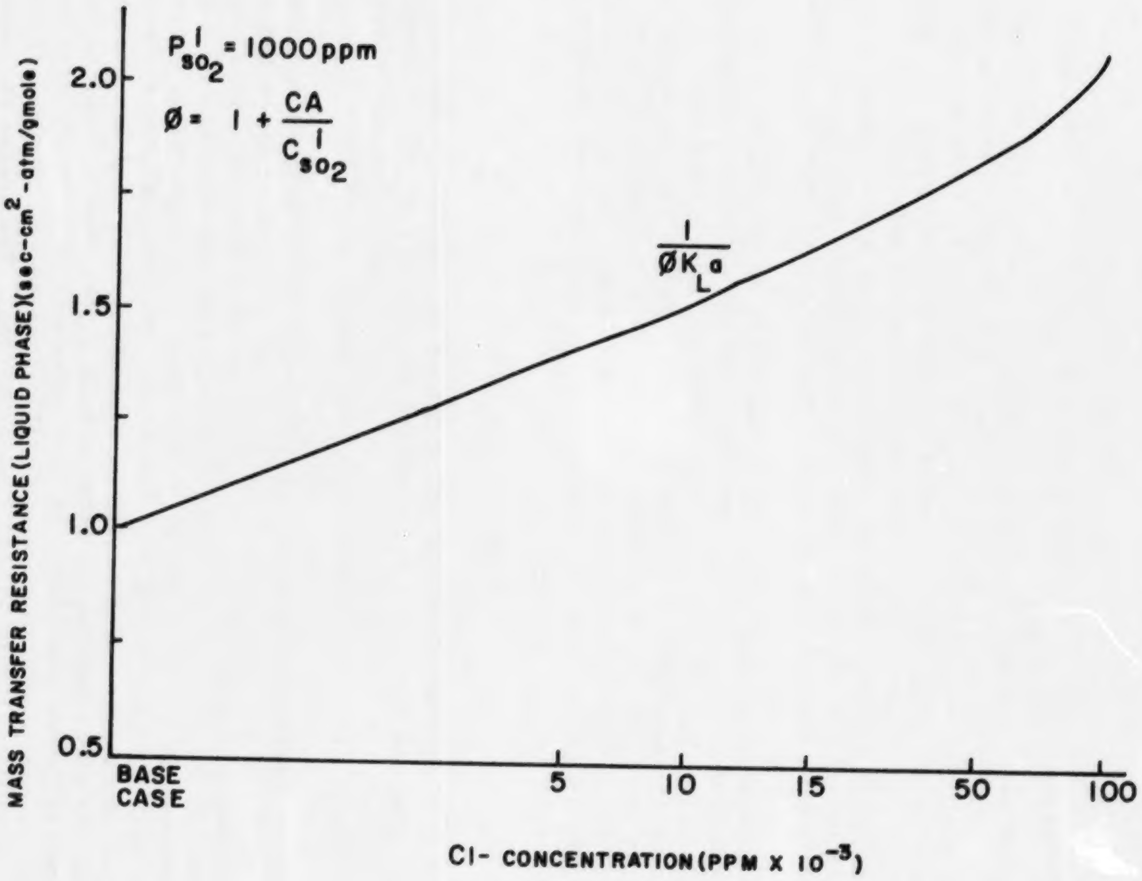


Figure 1. Calculated liquid phase mass transfer resistance vs. Cl$^-$ concentration.

Substituting Equation (14) into Equation (15)

$$\left(\frac{SO_4}{SO_3}\right)_{solid} = K'' \frac{(R.S.)^y}{\left(A_{Ca^{2+}}\right)^z} \qquad (16)$$

where $K'' = K'(K_{sp})^y$
$z = y - x$
$z > 0$

The expression, $\left(\frac{SO_4}{SO_3}\right)_{solid}$, represents the sulfate to sulfite ratio in the solid and should be a constant at a given oxidation level. Equation (16) indicates that if the oxidation level is fixed, the gypsum relative saturation will increase with the accumulation of calcium concentration (as a result of the increase in chloride ions) in order to maintain a constant $SO_4$ to $SO_3$ ratio in solids. In other words, higher gypsum scaling potential will result from the increase of calcium chloride. Furthermore, in the presence of a significant concentration of chloride ions, the subsaturated mode may be unobtainable and the scrubber will be forced into a supersaturated mode of operation.

Another impact of calcium chloride accumulation on scaling is a potential increase of the gypsum relative saturation across the absorber. Equation (14) indicates that with high calcium ion concentrations, the gypsum relative saturation level becomes very sensitive to changes in the sulfate concentration. At a high value of $A_{Ca^{2+}}$, a very small increase in the concentration of sulfate in the absorber (due to the oxidation by flue gas oxygen) may result in a significant rise in the calcium sulfate saturation level and may produce gypsum scale in the bottom of the absorber.

## TEST FACILITIES

In order to evaluate the effect of chlorides on the FGD system, a pilot plant test program was developed to determine the effects of high concentrations of chloride ions in the scrubbing liquor on scrubber operation; specifically $SO_2$ removal efficiency, limestone utilization, and scaling potential.

Two process configurations, natural and forced oxidation, shown in Figures 2 and 3, were employed for the tests. The scrubber, located at EPA's Industrial Environmental Research Laboratory in Research Triangle Park, NC, is a three stage turbulent contact absorber (TCA) with 7.5 $m^3$/min flue gas capacity (0.1 MW). No flyash was present in the flue gas which was drawn from a gas-fired boiler and injected with pure $SO_2$ and HCl as required. The oxidizer consisted of a 30 cm diameter tower containing slurry at a depth of 5.5 m and was sparged with air from the tower bottom. A bleed stream of the slurry from the hold tank was directed to the clarifier and then processed by a rotary drum vacuum filter to remove the precipitated waste. All filtrate was returned to the scrubber in order to maintain closed loop operation. The system was manually controlled in a feed forward mode by maintaining a constant stoichiometric ratio of moles of limestone added to the moles of $SO_2$ absorbed. A small

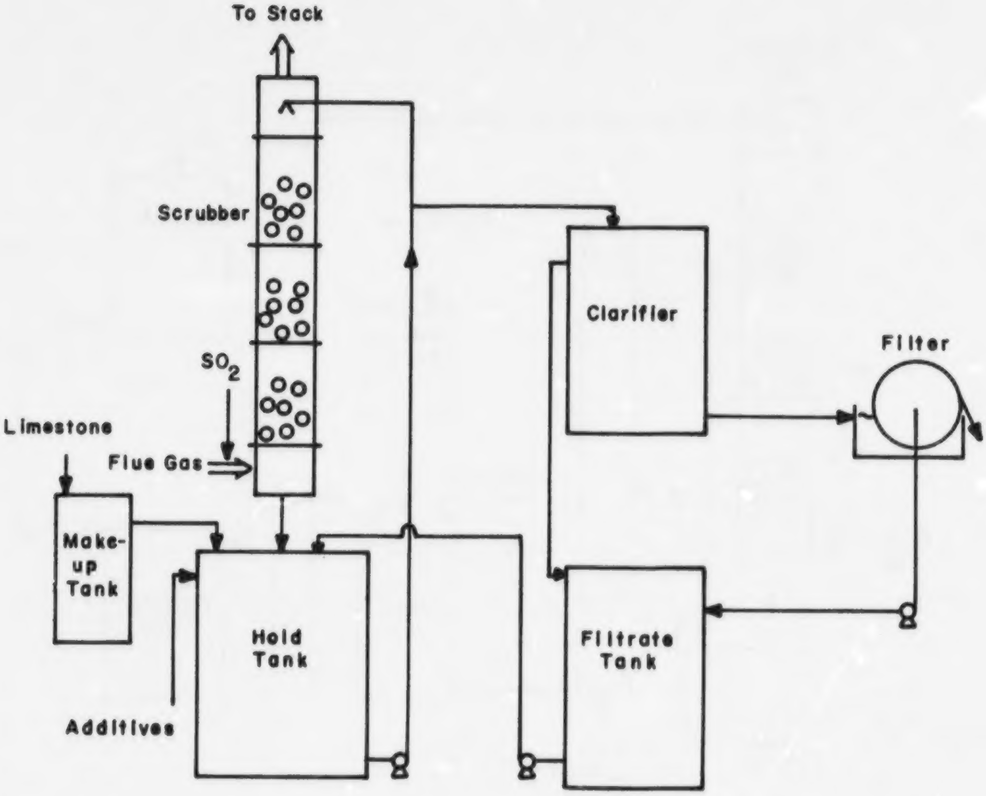


Figure 2. Flow diagram for single-loop natural oxidation tests in the 0.1 MW limestone pilot plant system.

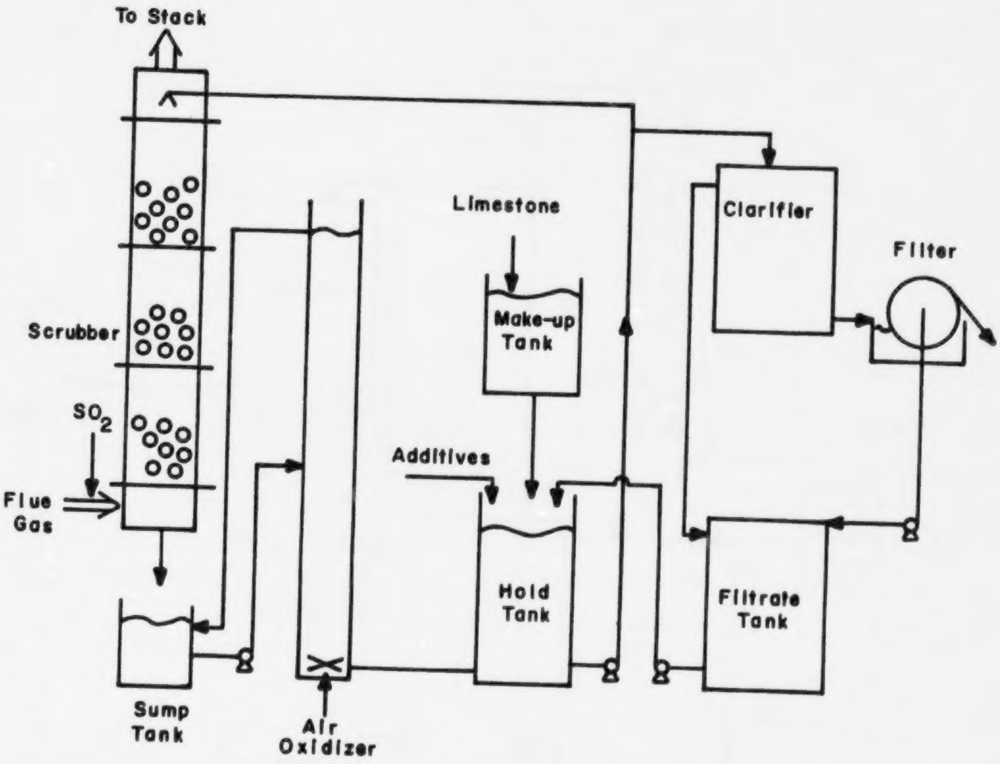


Figure 3. Flow diagram for the in-loop forced oxidation tests in the 0.1 MW limestone pilot plant system.

amount of excess limestone was also added in order to stoichiometrically neutralize the HCl gas absorbed.

The operating conditions listed in Table 2 were utilized for testing high concentrations of chlorides. Calcium chloride was added to the liquid inventory in order to bring the system to the desired chloride level at the beginning of each test. The gas phase HCl concentration at the scrubber inlet was controlled at the levels shown in Table 3. The limestone feed rate was adjusted manually by a trial and error method in order to reach steady state stoichiometric ratios. Each run consisted of at least 25 hours of continuous, stable operation, after which, scrubber performance and system conditions at each chloride level were established by averaging operational data logged hourly.

The gas phase sulfur dioxide concentration in the inlet and outlet of the scrubber was monitored continuously by ultraviolet spectrophotometry (DuPont 400 $SO_2$ analyzer) and wet gas analysis (titrimetric procedure)(22). The liquid phase chloride concentration was controlled by a chloride specific ion electrode and checked by ion chromatography and silver nitrate titration. Liquid and solid samples were taken regularly for the analysis of important species such as calcium, sulfite, sulfate, carbonate, magnesium and sodium.

## RESULTS AND DISCUSSION

The base case scrubber performance was established by results obtained without the addition of HCl and $CaCl_2$. An $SO_2$ removal efficiency of 79% and a hold tank pH of 6.0 were reached in the natural oxidation mode. With forced oxidation, the base case $SO_2$ removal efficiency was 80 percent with a hold tank pH of 5.9. The solids content of the recycle slurry was maintained at 10 percent. A subsaturated operation mode (with respect to gypsum) was obtained under natural oxidation with a relative saturation level of 50 percent in the hold tank and 70 percent in the scrubber effluent. The filter cake averaged 53 percent solids with natural oxidation and 78 percent solids with forced oxidation, and corresponded to hold tank slurry settling rates of 0.5 and 4.9 cm/min, respectively.

When the calcium chloride concentration was increased, the following significant changes in system performance were observed:

- A decrease in system pH
- A decrease in $SO_2$ removal efficiency
- A decrease in solids settling rate
- An increase in calculated gypsum saturation

Essentially the same trend of the chloride ion effect was observed for both the natural and forced oxidation conditions, but the effect of the $Cl^-$ concentration was less severe with forced oxidation than with natural oxidation. At the same chloride level, scrubber performance of forced oxidation was always superior to that of natural oxidation, although the higher percent solids in the filter cake of forced oxidation systems will increase steady state chloride levels much higher than a natural oxidation system. This increase tends to counteract the benefits of forced oxidation over natural oxidation.

## TABLE 2. PILOT PLANT OPERATING CONDITIONS

Absorber = Turbulent Contact Absorber with 3-7" static beds, 1 1/2" spheres

Liquid to Gas Ratio = 60 gpm/1000 acfm (8 $l/m^3$)

Flue Gas $SO_2$ Concentration = 2500 ppm

Flue Gas HCl Concentration = 0-400 ppm

Flue gas $O_2$ Concentration = 9-11 percent

Limestone stoichiometry = 1.35 (natural oxidation), 1.2 (forced oxidation)

Hold Tank Solids Concentration = 10 weight percent

Hold tank residence time = 11.5 minutes

Oxidizer $O/SO_2$ ratio = 2.8 (forced oxidation only)

## TABLE 3. FLUE GAS HCl CONCENTRATION

| Operation Mode | Natural Oxidation | | Forced Oxidation | |
|---|---|---|---|---|
| Liquid Cl Concentration (g/l) | Base Case 0, | 20, 30, 40, 50, 100 | Base Case 0, | 50, 80, 180 |
| Gas Inlet HCl (ppm) | 0, | 150, 230, 280, 310, 350 | 0, | 150, 230, 370 |

## EFFECT OF $Cl^-$ ON SYSTEM pH

A comparison of natural and forced oxidation hold tank pH's obtained at various chloride concentrations is shown in Figure 4. The drop of pH with forced oxidation was not significant until $Cl^-$ exceeded 50,000 ppm, which confirmed previous data by Borgwardt(6). A hold tank pH of 5.2 was obtained at 180,000 ppm of $Cl^-$ with forced oxidation; while the same pH drop was observed at only 30,000 ppm $Cl^-$ with natural oxidation. A comparison of natural oxidation hold tank pH data with the theoretical prediction (Equations (1) and (2)) is shown in Figure 5. The good agreement confirms that chloride ions affect the system pH as predicted. Two data points obtained previously by Borgwardt(6) are also presented in Figure 5 for reference.

## EFFECT OF $Cl^-$ ON $SO_2$ REMOVAL

Results of changes in $SO_2$ removal efficiency as a function of the chloride ion concentration are shown in Figure 6. For forced oxidation, the change of $SO_2$ removal efficiency was insignificant at $Cl^-$ concentrations below 50,000 ppm, which was in accordance with $Cl^-$ effect on the hold tank pH. The sharp drop of $SO_2$ removal under natural oxidation, accompanied by the decrease of the hold tank pH, reflects the reduction of dissolved alkalinity by $Ca^{2+}$ and $Cl^-$ accumulation as discussed in the theoretical analysis. At the same $Cl^-$ level, a higher $SO_2$ removal efficiency was always obtained with forced oxidation. But the difference between forced and natural oxidation data can not be fully explained by the effect of the hydrolysis reaction. Other factors related to the mass transfer rate, such as limestone dissolution and calcium sulfite saturation level should also be considered in interpreting the data.

In one test, the flue gas HCl injection was stopped for eight hours in order to evaluate the effect of gas phase HCl concentration on the $SO_2$ scrubber performance at 100,000 ppm $Cl^-$. No significant changes in the hold tank pH were observed but the $SO_2$ removal efficiency increased from 32 to 36.5 percent under natural oxidation conditions due to the decrease in total acidic gas concentration. Compared with the drop of $SO_2$ removal from the base case (from 79 to 32), the change caused by gas phase HCl concentration is insignificant. The data confirm that liquid phase calcium chloride accumulation is the major direct cause of decreasing $SO_2$ removal.

## EFFECT OF $Cl^-$ ON THE SOLID SETTLING RATE

The settling rate reported is the three minute average descending rate of the miniscus between the clear supernate and the turbid zone of the hold tank slurry sample in a 100 ml graduated cylinder. Figure 7 indicates that under natural oxidation conditions, more than a 40 percent drop of the solid settling rate was observed with an increase in the chloride concentration from the base case to 20,000 ppm and decreased further as calcium chloride accumulated. As shown in Figure 8, with forced oxidation, no significant change of settling rate was observed - with the one exception at a concentration of 180,000 ppm $Cl^-$. During this test, the settling rate dropped drastically by one order of magnitude (from about 4 to 0.9 cm/min) as the chloride concentration increased from 80,000 to 180,000 ppm, but the solids content of the filter cake remained constant.

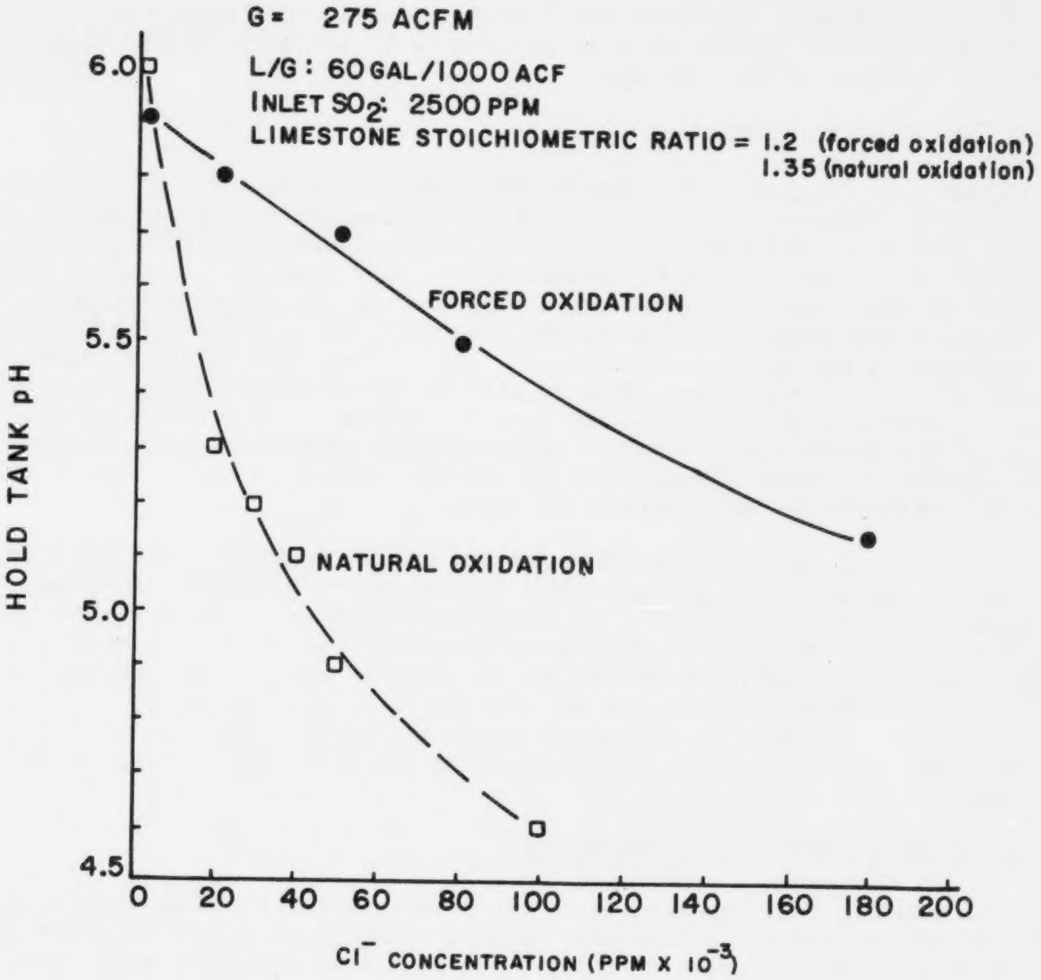


Figure 4. Comparison of natural and forced oxidation hold tank pH's.

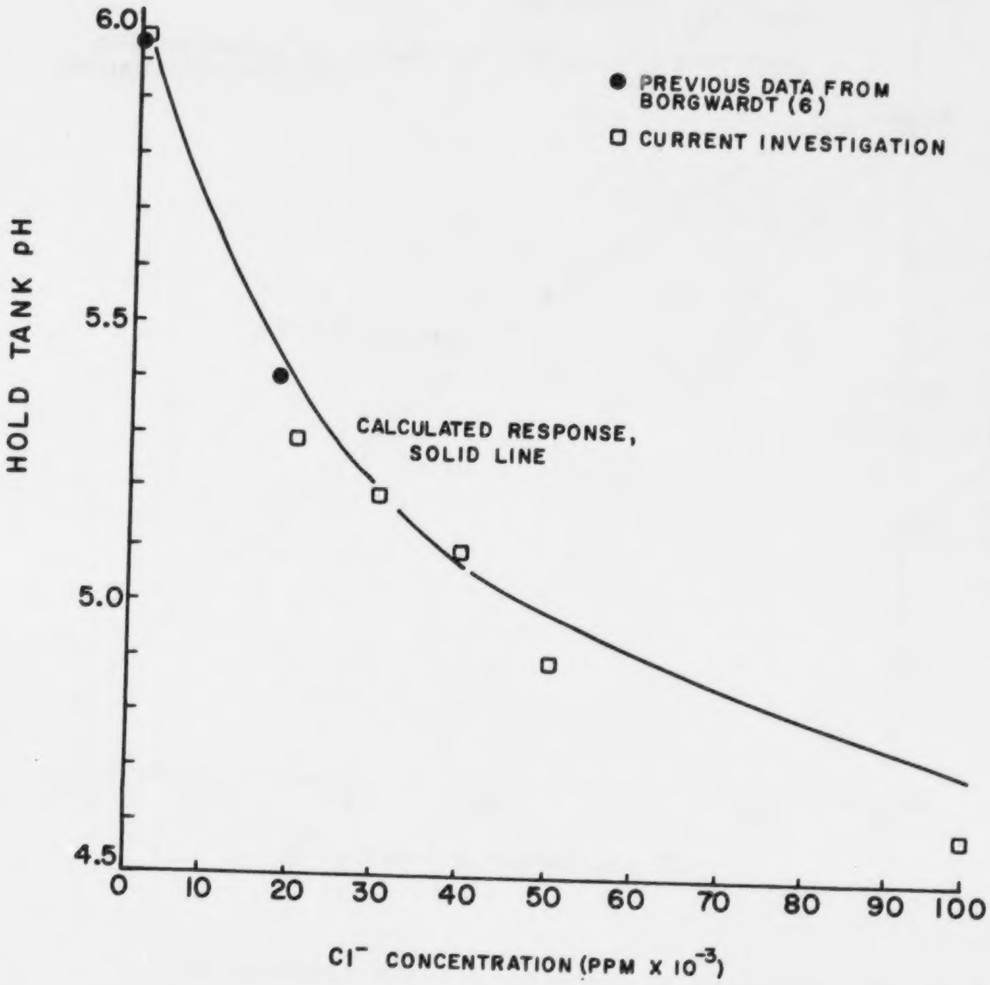


Figure 5. Comparison of natural oxidation hold tank pH data with calculated response.

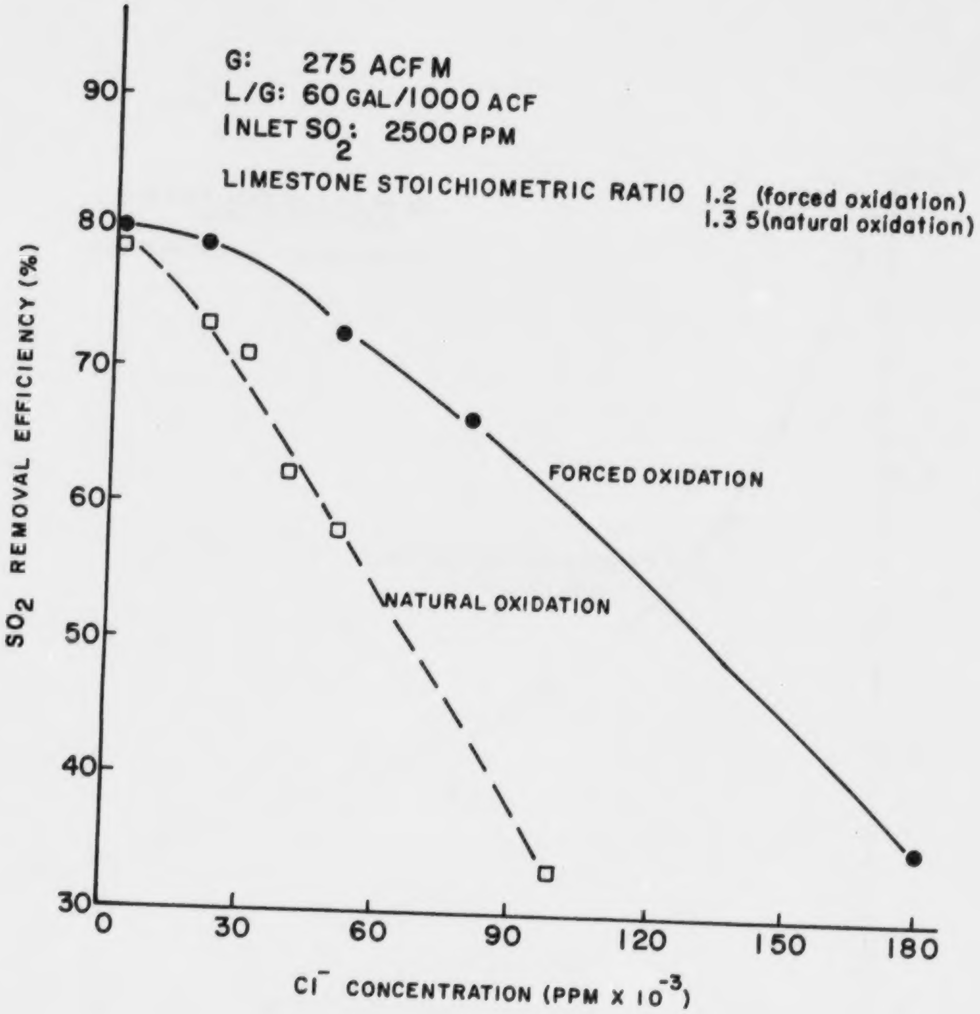


Figure 6. Comparison of natural and forced oxidation $SO_2$ removal efficiencies as a function of slurry chloride concentration.

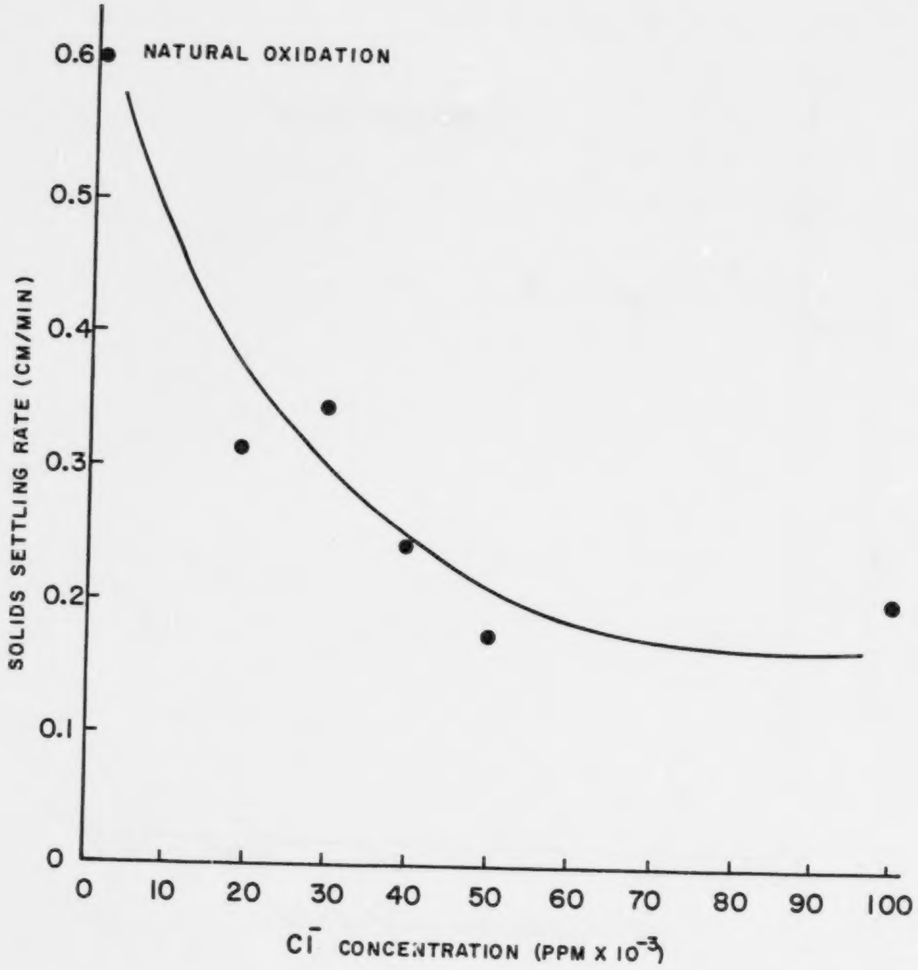


Figure 7. Chloride effect on $SO_2$ scrubber performance: solids settling rate vs. $Cl^-$ concentration.

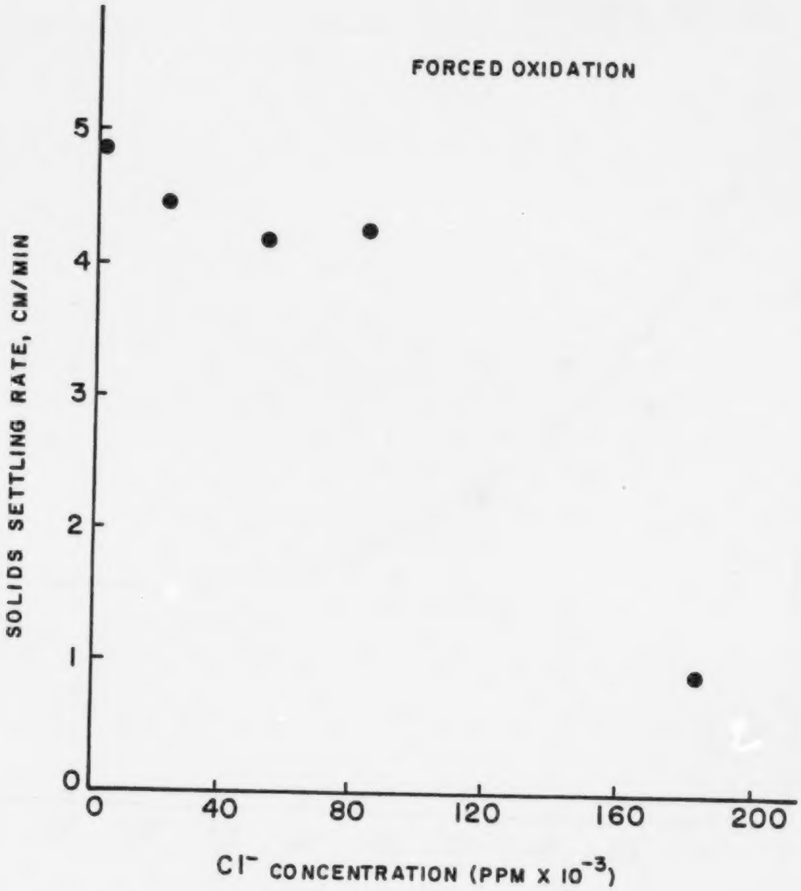


Figure 8. Chloride effect on $SO_2$ scrubber performance: solids settling rate vs. $Cl^-$ concentration.

An analysis of the unoxidized filter cake for the presence of solid chlorides was performed with unwashed and thoroughly washed filter cake samples. Results have indicated that washing the cake three times is sufficient to extract 80% of the chlorides, indicating little solid phase chlorides. The chloride content of the washed filter cake was usually below 7 mg per gram of dry solid.

## EFFECT OF $Cl^-$ ON GYPSUM SCALING POTENTIAL

By measuring concentrations of major chemical species such as calcium, sulfite, sulfate, magnesium, sodium and chloride in slurry samples taken from the hold tank and scrubber effluent, the calcium sulfate relative saturation level was estimated by the use of the Bechtel Modified Radian equilibrium computer program. Data shown in Figure 9 indicate that subsaturated operation is not sustained at high chloride concentrations. The calcium sulfate relative saturation in the hold tank fluctuated near the 100 percent level with chloride concentration above 20,000 ppm, and the saturated operation mode prevailed. Solids analysis indicated that the oxidation was maintained at a constant level (between 10 and 15 percent) regardless of the chloride concentration for most runs. This is in accordance with the previous analysis that high calcium chloride concentrations may raise the gypsum relative saturation ratio and force the limestone scrubber into a saturated operation mode. The data shown in Figure 10 indicate the calcium sulfate saturation level was always higher than 130 percent in the scrubber effluent and the gypsum scaling potential was considerably higher with increased chloride concentrations. However, no serious scaling was observed in the pilot plant, possibly due to the short term nature of the tests.

## EXPERIMENTAL METHODS ATTEMPTED TO COUNTERACT THE EFFECTS OF CHLORIDES

Short term pilot plant tests were conducted in an effort to evaluate methods which might offset the observed effect of chlorides and thereby raise $SO_2$ removal efficiency.

The effectiveness of a high limestone stoichiometry was tested under natural oxidation conditions. Excess limestone was added to the hold tank in order to raise the system pH and $SO_2$ absorption rate. Data shown in Figure 11 indicate that an extremely high limestone stoichiometry is required to offset the depressed $SO_2$ removal efficiency. At 40,000 ppm $Cl^-$, the limestone feed rate had to be increased by more than 200 percent to reach the base case $SO_2$ removal. A high L/G ratio was also tested, since it not only raises the $SO_2$ removal efficiency but also alleviates gypsum scaling in scrubber bottom through reduced make-per pass. Test results indicate that at 40,000 ppm chloride, the L/G had to be doubled in order to offset the $Cl^-$ effect on $SO_2$ removal efficiency (Figure 12).

The use of mass transfer additives to increase dissolved alkalinity was also considered. Decreasing the $Ca^{2+}$ concentration by the introduction of other cations such as magnesium (or sodium) will be tested in the future. An organic acid was considered a more attractive additive than magnesium since previous data indicate it is very effective in enhancing the $SO_2$ removal efficiency of limestone scrubbers.(23) Organic acids are present in the limestone slurry as anions which react with the acidity generated by $SO_2$ absorption and enhance the $SO_2$ removal efficiency in a method similar to increasing dissolved alkalinities. Calculations indicate that the maximum

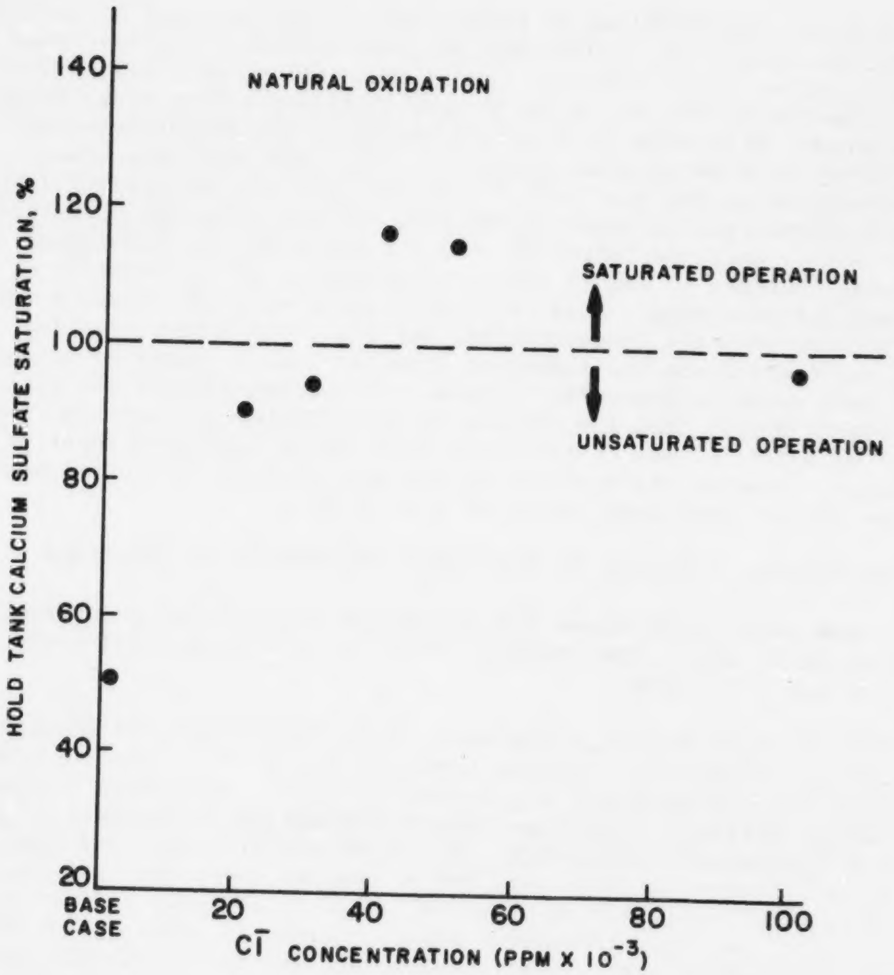


Figure 9. Chloride effect on $SO_2$ scrubber performance: hold tank calcium sulfate saturation vs. Cl- concentration.

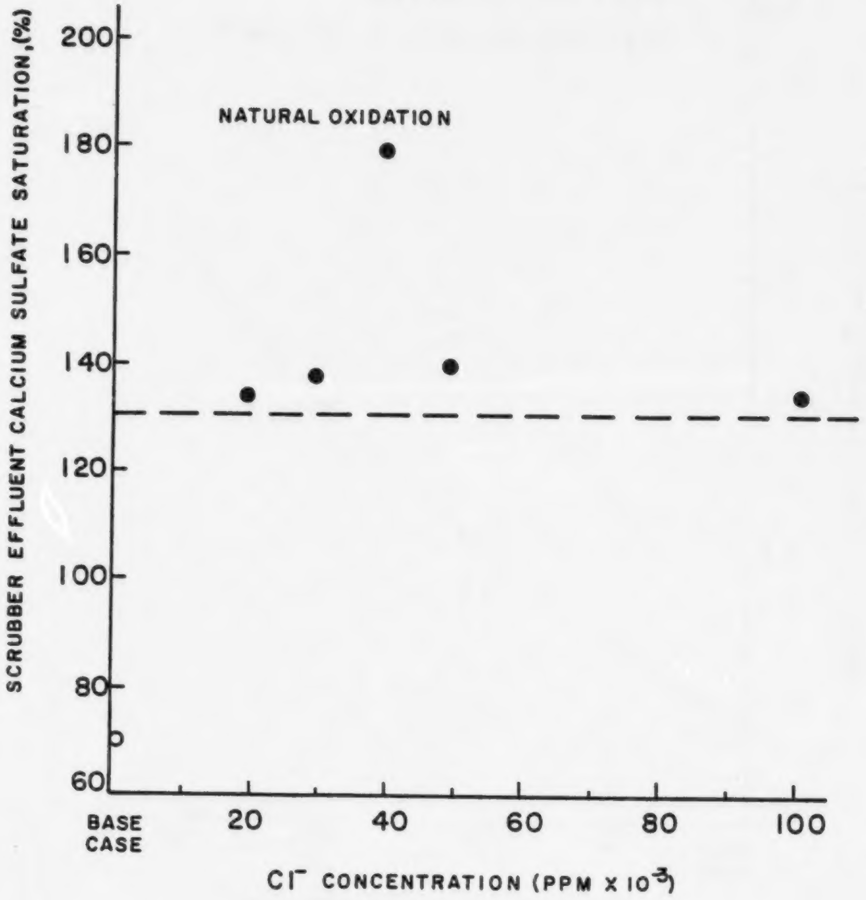


Figure 10. Chloride effect on $SO_2$ scrubber performance: scrubber effluent calcium sulfate saturation vs. $Cl^-$ concentration.

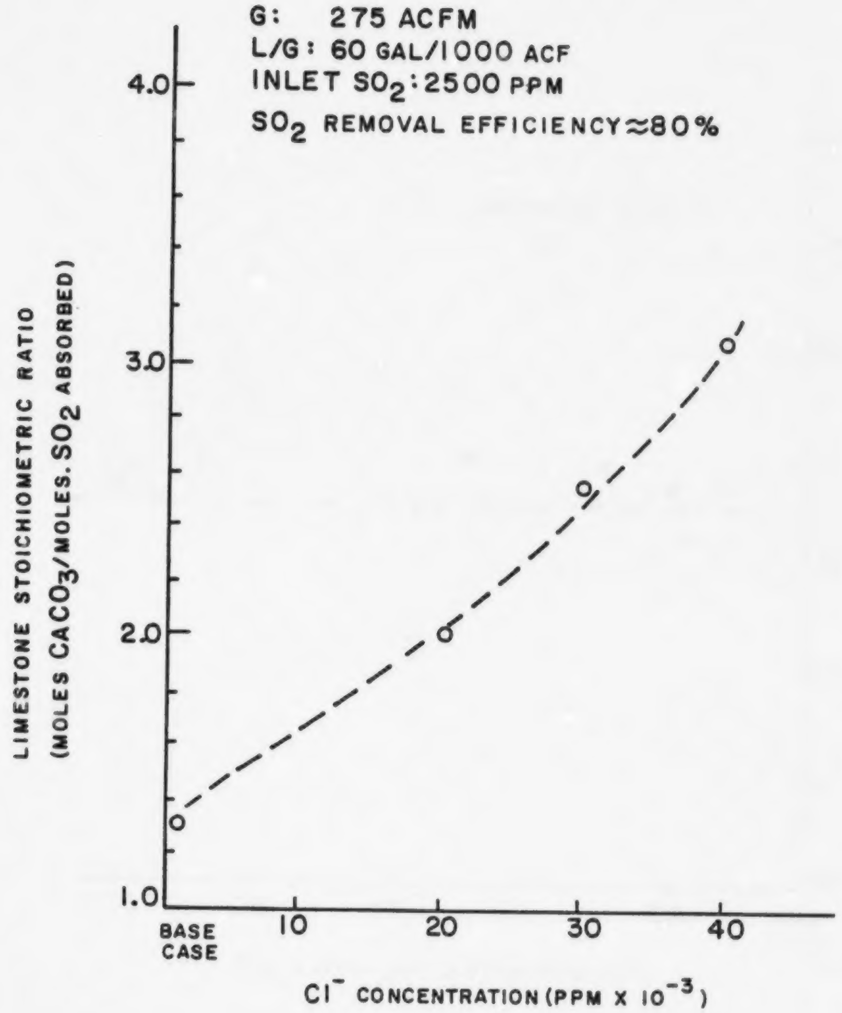


Figure 11. Limestone stoichiometric ratio required for 80% $SO_2$ removal vs. $Cl^-$ concentration with natural oxidation.

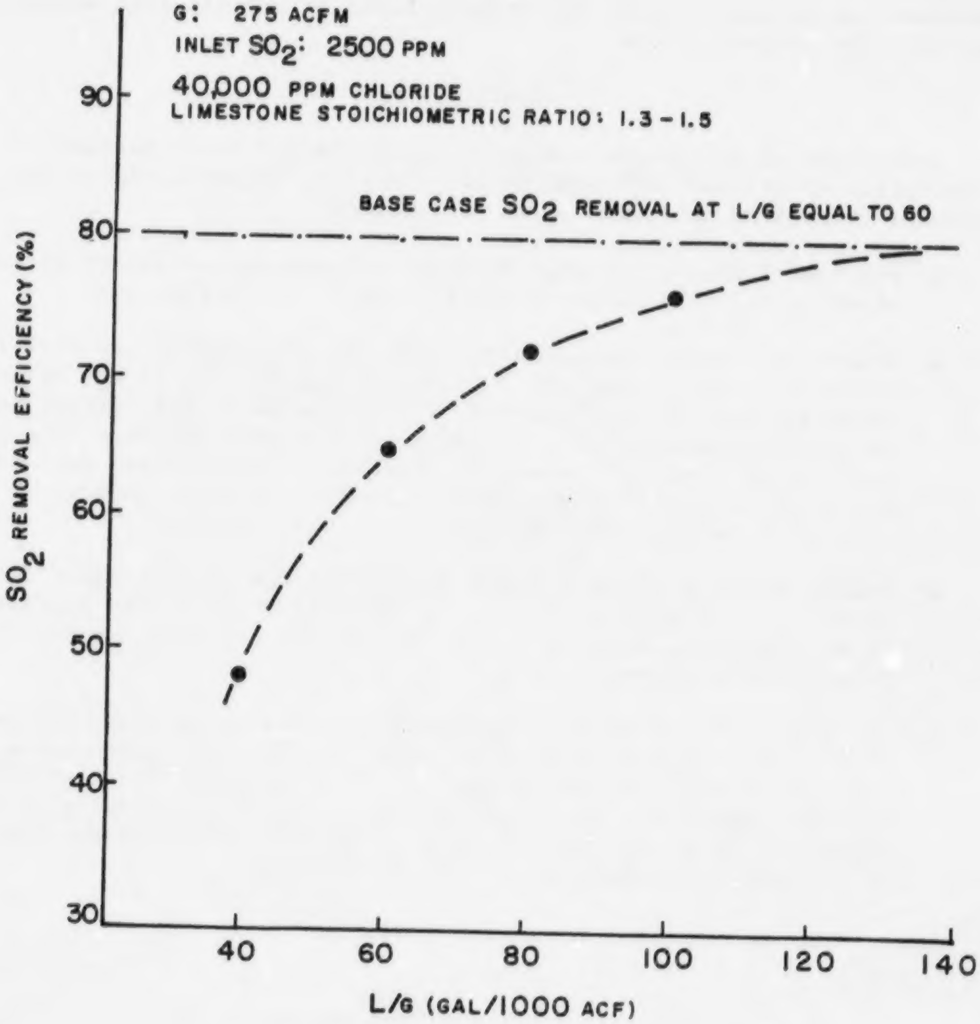


Figure 12. Effect of L/G ration on $SO_2$ removal at 40,000 ppm chloride level with natural oxidation.

organic acid concentration required to offset depleted alkalinity due to $CaCl_2$ accumulation will be less than 10 mM. Pilot plant data shown in Figure 13 indicate that only 9 meq/l of total organic acid (or equivalently 650 ppm of adipic acid) was needed to restore the $SO_2$ removal efficiency to the base case efficiency at 50,000 ppm $Cl^-$ with natural oxidation. Tests are under consideration to characterize the effectiveness of organic acid additives at high chloride concentrations.

## CONCLUSIONS

Absorption of HCl gas in the pilot plant TCA and the subsequent accumulation of $Cl^-$ and $Ca^{2+}$ ions in the absorbing liquor produced the following effects on the pilot plant performance:

- Absorber hold tank pH decreased as $Ca^{2+}$ and $Cl^-$ increased and was shown to follow calculated equilibrium $H^+$ concentrations.
- A decrease in $SO_2$ removal efficiency was observed in the forced oxidation mode at approximately 50,000 ppm $Cl^-$ and in the natural oxidation mode at approximately 20,000 ppm $Cl^-$. This effect was partially attributed to a decrease in dissolved alkaline ions in equilibrium with $Ca^{2+}$ ions. $SO_2$ removal efficiency was restored in the natural oxidation mode by the addition of small amounts of organic acid or by adding large amounts of excess limestone.
- Solids settling rates declined as the $Cl^-$ ion concentration increased in the natural oxidation mode. Little effect on solids settling due to chlorides was observed under 180,000 ppm $Cl^-$ when running in the forced oxidation mode.
- The relative saturation of gypsum in the system increased to levels conducive to high scaling potential. The rise was shown to be a function of $Ca^{2+}$ concentration. Also, scaling potential at the scrubber bottom was predicted due to increased sensitivity of the absorbing liquor to small changes in $SO_4^{2-}$ concentration; however, little scale was observed in the pilot plant.

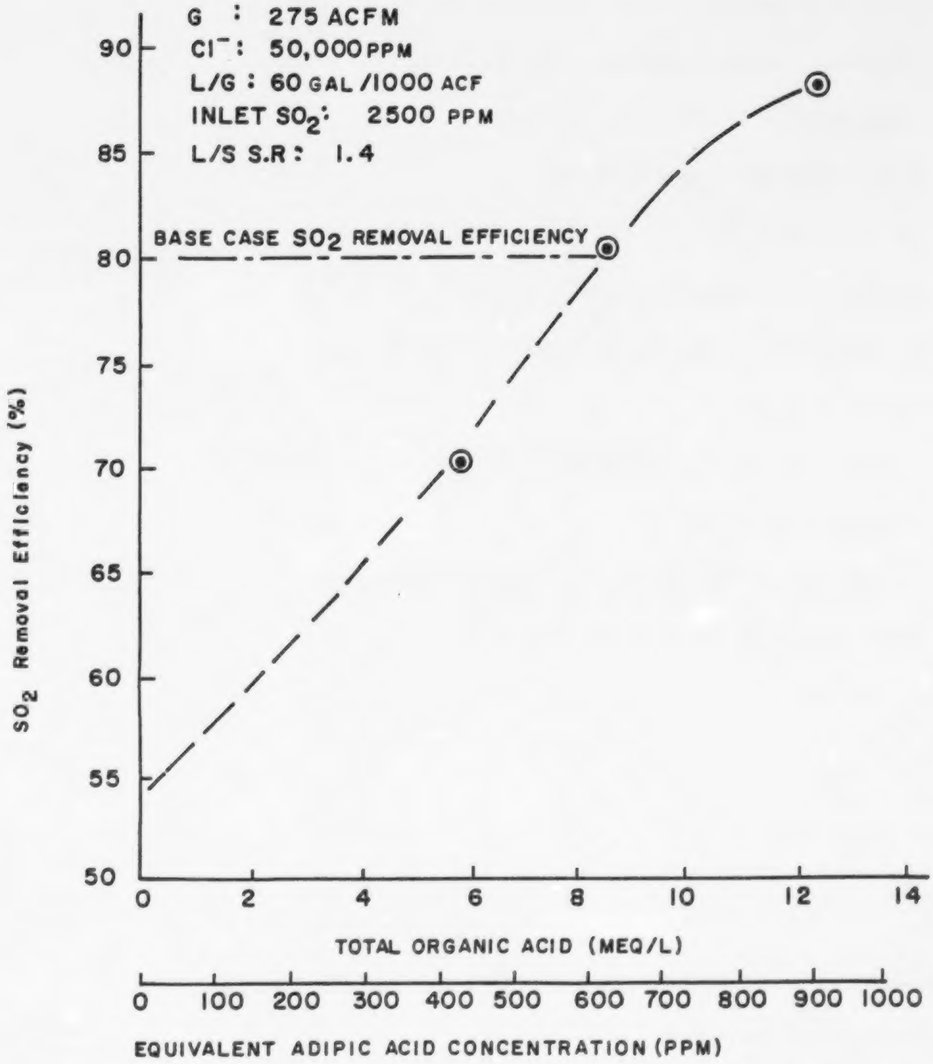


Figure 13. Effect of organic acid concentration on sulfur dioxide removal at 50,000 ppm chloride with natural oxidation.

# NOTATION

$A$ = component activity, gmole/liter

$C$ = component concentration, gmole/liter

$D$ = component diffusivity, $cm^2/sec$

$I$ = ionic strength, gmole/liter

$K_L$ = liquid-phase mass transfer coefficient, $liter/sec\text{-}cm^2$

$K_{sp}$ = solubility product, $(gmole/liter)^2$

$K'$ = correlation constant in Equation (15)

$n$ = ionic valence

$N$ = molar flux, $gmole/sec\text{-}cm^2$

$P$ = partial pressure, atm

$\alpha$ = parameter in Equation (4), gmole/liter-atm

$\phi$ = mass transfer enhancement factor

Subscript

$A$ = alkalinity

$j$ = jth component

$w$ = water

Superscript

$i$ = gas-liquid interphase

$o$ = bulk liquid

$x$ = correlation parameter in Equation (15)

$y$ = correlation parameter in Equation (15)

# REFERENCES

(1) Evers, R., V. E. Vandergriff, R. L. Zielke, "Field Study to Obtain Trace Element Mass Balances at a Coal-fired Utility Boiler", EPA-600/7-80-171, October, 1980.

(2) Personal Communication with B. Laseke, PEDCo Environmental, March 1, 1982 by D. Laslo.

(3) PEDCo Environmental, Inc., "Survey of Design and Actual Chloride Levels in Commercial Closed Water Loop FGD System", Prepared under contract for Peabody Process Systems, Inc., unpublished, Feb, 1982.

(4) Head, H., "EPA Alkali Scrubbing Test Facility: Advanced Program, Third Progress Report", EPA-600/7-77-105, September, 1977.

(5) Burbank, D. A., S. C. Wang, "EPA Alkali Scrubbing Test Facility: Advanced Program - Final Report (October 1974 - June 1978)," EPA-600/7-80-115, May, 1980.

(6) Borgwardt, R. H., "Effect of Forced Oxidation on Limestone/$SO_x$ Scrubber Performance", Preceedings: Symposium on Flue Gas Desulfurization, Hollywood, FL, EPA 600-7-78-058a, p205, 1978.

(7) Rochelle, G., "Limestone Dissolution in Aqueous Solution," EPA Grant R806351, Monthly Progress Report, June, 1981.

(8) Rader, P. C., R. W. Hanson, D. C. Borsare, "Design of Lime/Limestone Flue Gas Desulfurization Systems for High Chlorides". Presented at Coal Technology '81, Houston, TX, November, 1981.

(9) Personal communication with P. Rader by D. Laslo on 11/20/81.

(10) Furuta, I., "Desulfurization Process," United States Patent 3,959,441, May 25, 1976.

(11) Borgwardt, R. H., "Combined Flue Gas Desulfurization and Water Treatment in Coal Fired Power Plants", Environmental Science & Technology, Vol. 14, No. 3, p 294-298, March, 1980.

(12) Koch, G. H., J. A. Beaver, N. G. Thompson, W. E. Berry, "A Survey of the Performance of Candidate Construction Materials for Flue Gas Desulfurization Systems", Draft of report prepared for Electric Power Research Institute, (To be published in May, 1982).

(13) Koch, T. H., J. A. Beaver, "The Experimental Evaluation of Alloys and Linings in Simulated Duct Environments for a Lime/Limestone Scrubber", DRAFT EPRI-1871-1, July, 1981. (To be published in May, 1982).

(14) Rochelle, G. T., and C. J. King, "The Effect of Additives on Mass Transfer in $CaCO_3$ or CaO Slurry Scrubbing of $SO_2$ From Waste Gases", Ind. Eng. Chem. Fund., 16, 67 (1977).

(15) Onda, K., E. Sada, T. Kobayaski, S. Kito, and K. Ito, "Salting-Out Parameters of Gas Solubility in Aqueous Salt Solutions", Journal of Chemical Engineering of Japan, 3, 1, 18, 1970.

(16) Ratcliff, G. A., and J. G. Holdcroft, "Diffusivities of Gases in Aqueous Electrolyte Solutions", Trans. Inst. Chem. Engrs., 41, 315, 1963.

(17) Chang C. S., and G. T. Rochelle, "$SO_2$ Absorption into Aqueous Solutions," AIChE Journal, 27, 2, 292, 1981

(18) Hatfield, J. D., and A. V. Slack, "Sulfur Removal and Recovery from Industrial Processes", Advances in Chemistry Series 139, American Chemical Society, p. 130, 1975.

(19) Lowell, P. S., D. M. Ottmers, K. Schwitzgebel, T. I. Strange, and D. W. Deberry, P. G. 193-029, U.S. Environmental Protection Agency, 1970.

(20) Chang, C. S., and G. T. Rochelle, "Effect of Organic Acid Additives on $SO_2$ Absorption into $CaO/CaCO_3$ Slurries", AIChE Journal, 28, 2, 261, 1982

(21) Rader, P. C., D. C. Borio, S. L. Goodstine and M. R. Gogineni, "The Role of Crystallization in the Design of Lime/Limestone Wet Scrubbing Systems for Flue Gas Desulfurization", Presented at the 83rd National AIChE Meeting in Houston, March, 1977.

(22) Morris, K., "Methods of Air Sampling and Analysis", 2nd Ed, p737, American Public Health Association, 1977.

(23) Mobley, J. D. and C. S. Chang, "The Adipic Acid Enhanced Limestone Flue Gas Desulfurization Process, An Assessment", JAPCA, 31, 12, 1249, 1981.

# FGD CHEMISTRY AND WATER INTEGRATION

by: Dorothy A. Stewart
Electric Power Research Institute
Palo Alto, CA 94303

O. W. Hargrove
Radian Corporation
Austin, TX

## ABSTRACT

The electric utility industry is interested in power plant water management to both conserve water and reduce waste water discharge to a minimum. For those power plants operating flue gas desulfurization (FGD) systems, the water management becomes more complex, but utilization of waste water in the FGD system is possible. Calculations of the effects of the various waste water streams on operation of lime and limestone wet scrubbing processes have shown that in many cases the $SO_2$ removal is enhanced by using these streams as makeup water to the system. The results of calculations using various combinations of makeup water, reagents, and flue gas compositions are given in this paper.

## INTRODUCTION

The Electric Power Research Institute has initiated studies in flue gas desulfurization (FGD) lime and limestone process chemistry. The goals of this work are to improve performance and reliability of FGD and to produce a reliable model of these processes. Investigations are currently being conducted to determine effects on process chemistry of:

- Reagent Properties - to improve performance.
- Reagent Preparation - to increase reagent utilization and $SO_2$ removal.
- High Total Dissolved Solids - to improve FGD system tolerance.

- Crystallization Conditions - to improve solids handling properties.
- Integration of FGD with Plant Water System - to decrease water usage and wastewater discharge.

This paper presents the results of the initial work on the integration of plant water systems with the FGD process.

Increasingly stringent environmental regulations and water shortages in the West and in some locations in the East create the need for increased water recycle/reuse in steam electric power plants. A fully integrated, cascading water system is necessary to minimize water discharge, but the process chemistry must be controlled carefully to ensure that reliable operation and satisfactory performance are achieved in water systems throughout the plant. In coal-fired power plants, the FGD system, as a net consumer of water, plays a key role in water management systems designed to minimize effluents through water recycle/reuse. Because of the importance of water management and the possible effects integration may have on the FGD process chemistry, EPRI commissioned Radian Corporation to investigate potential effects of different process waters and water treatment schemes on the process chemistry of lime and limestone FGD systems.

## EXPERIMENTAL PROCEDURE

Radian employed its Process Simulation Model to predict the effects of different process water compositions on FGD system chemistry in both eastern coal (10,100 Btu/lb and 4.0 percent sulfur) and western coal (8,080 Btu/lb and 0.48 percent sulfur) applications. The water sources selected for study included Santee River water (76 mg/l total dissolved solids [TDS]), Mississippi River water at St. Louis (457 mg/l TDS), and Lake Sakajawea water (3500 mg/l TDS). Two systems of cooling tower operation were also simulated using Lake Sakajawea and Mississippi River water as makeup, and the cooling tower blowdown streams were used as alternative makeup sources for the FGD system. Low-volume wastewater streams (demineralizer regeneration waste and pretreatment softener clarifier blowdown) were also briefly examined as supplemental makeup water to the FGD system. The cases were designed so that a cross-section of possible operating conditions was examined in both eastern and western coal cases.

Other important chemical variables such as reagent selection (lime or limestone), reactive magnesium content of the reagent, and coal chloride content were also investigated. The effects of relatively high and low reactive magnesium content in reagent sources on the FGD system were examined. The $Mg(OH)_2$ concentrations for the two lime studies were 1.66 and 0.55 wt.%. The reactive $MgCO_3$ contents for the limestones were 1.5 and 0.15 wt.%. Coal chloride content was studied for western and eastern coals containing 0.03 wt.% chlorine and 0.1 wt.% chlorine, respectively. Another eastern coal containing 0.3 wt.% chlorine was also studied to measure the effect of increased chloride concentration on FGD system process chemistry.

The primary chemical effects investigated for FGD system operation were (1) the alkalinity (concentration of species which react with $SO_2$) required to meet $SO_2$ absorption requirements and (2) the system's chemical scaling tendency. A spray tower system with a single reaction tank was the design used to examine effects on a consistent basis. In each case, the liquid-to-gas (L/G) ratio was determined based on the alkalinity required to achieve the desired $SO_2$ absorption, and the reaction tank was then sized to provide non-scaling conditions in the absorber. In one particular case, the process makeup water was changed for a fixed system design, and the $SO_2$ removal efficiency and gypsum scaling tendency were predicted for different makeup water sources to determine effects of changing water supplies.

The objective of this project was to compare the effects on process chemistry of changing makeup water and other important chemical variables. (The results of this study should be used only for comparison of effects and should not be applied to actual design applications since important properties such as physical $SO_2$ mass transfer limitations were not considered.) Because L/G was allowed to vary with conditions, unrealistic L/G ratios for spray towers were simulated (less than 30 gal/Macf in some western cases and greater than 200 gal/Macf in some eastern cases). In an actual design, the use of absorbers in series or grid towers would be considered in arriving at the optimum FGD system design.

Caution should be exercised before applying these results directly to an operating situation for some of the cases studied. While the Radian model has been extensively examined at solution ionic strengths less than 1.5, there are only limited data at higher strengths, and there is, accordingly, less confidence in the absolute model predictions under these conditions. However, the trends predicted by the model should be valid for comparative purposes and to provide insight into the process chemistry trends.

## RESULTS

The major effect of alternate water sources, reagent magnesium content, or coal chloride content on $SO_2$ scrubber performance is on the liquid phase alkalinity and the resulting L/G required for $SO_2$ sorption. These chemical variables caused L/G to change by as much as a factor of 8 and resulted in a variation in the reaction tank size of up to 20 percent. The reaction tank sizing criteria were the amount of $SO_2$ absorbed, the fraction of $SO_2$ oxidized, and the composition of the solids precipitated (gypsum or calcium sulfite/sulfate solid solution).

The effect of liquid phase alkalinity on L/G is summarized in Figure 1 for both eastern and western coal FGD systems. In general, the L/G in an eastern coal FGD system design will be higher than a western coal design because the $SO_2$ removal requirement is significantly higher as is the mass of $SO_2$ removed--90 percent removal from firing a 4.0 percent sulfur coal compared to 70 percent removal from a 0.48 percent sulfur coal. With a consistent coal composition, however, the liquid phase alkalinity is the primary variable which influences the L/G requirement.

In systems operating without organic additives, the liquid phase alkalinity is affected by the concentrations of such soluble species as magnesium, sodium, and chloride. Magnesium and sodium tend to hold alkaline species in solution while chloride tends to displace the less soluble alkaline species (e.g., sulfite and carbonate) from solution. As a result, systems which operate with (1) high concentrations of reactive magnesium in the reagent, (2) process makeup water high in magnesium and sodium concentrations relative to chloride, and (3) relatively low coal chloride concentrations require lower L/G to achieve an equivalent $SO_2$ removal efficiency. Figure 1 shows that these effects result in differences in L/G of a factor of 3 for the eastern cases and a factor of 8 in the western cases.

## EFFECT OF MAKEUP WATER SOURCE

The main effect of a change in process makeup water is to alter the liquid phase alkalinity, although the process chemistry changes may also modify the FGD system's scaling tendency. The results of using different process waters in an eastern coal limestone FGD application are summarized in Table 1.

TABLE 1. EFFECT OF PROCESS MAKEUP WATER ON AN EASTERN LIMESTONE FGD SYSTEM

| Makeup Water | L/G Ratio (gal/1000 acf) | Reaction Tank Size (1000 gal) | Absorber Feed TDS (1000 ppm) |
|---|---|---|---|
| Santee River | 135 | 739 | 18 |
| Lake Sakajawea | 96 | 772 | 28 |
| Mississippi River | 133 | 746 | 19 |
| Mississippi River: cooling tower/acid addition | 127 | 749 | 20 |
| Mississippi River: cooling tower/sidestream softening | 78 | 799 | 46 |

Using blowdown from a cooling tower using Mississippi River water with lime/soda ash sidestream softening as makeup to an FGD system results in the highest liquid phase alkalinity (0.01 N) and lowest L/G (78 gal/Macf). The liquid phase alkalinity for the sidestream softened cases is substantially greater than for the acid addition case. The sodium added in the form of soda ash in the softening step results in a much more alkaline scrubbing solution. This demonstrates that high TDS makeup water is not necessarily detrimental to FGD system performance. However, the full effects on the process chemistry of all unit operations should be considered before making a decision on process water for a specific FGD application. It should be noted that in general these simulations considered the process chemistry of the absorber and reaction tank and not the chemistry associated with the mist eliminator or other equipment.

Lake Sakajawea water is the most alkaline of the untreated makeup waters, and the FGD system L/G was only 96 gal/Macf compared to about 135 gal/Macf for the other untreated waters and 78 gal/Macf for the sidestream softened case discussed above. Again, this water had the highest TDS level of any of the untreated water sources considered in this study.

The process chemistry differences in the cases shown in Table 1 result in differences in reaction tank size of only about 8 percent for these eastern coal limestone applications. The sidestream-softened Mississippi River water requires the largest reaction tank--799,000 gallons.

The effects of process makeup water source in the western coal application are summarized in Table 2. The most noticeable difference between eastern and western coal cases are the lower L/G and smaller reaction tanks for the western cases. These differences are a direct result of the lower $SO_2$ concentration in the flue gas and lower required $SO_2$ removal efficiency (70 percent compared to 90 percent for the eastern case) in the Western cases. As an example, consider the untreated Mississippi water cases. In the eastern coal situation (Table 1), the L/G required was 133 gal/Macf and the reaction tank was 746,000 gallons. Table 2 shows the corresponding values for the western coal situation to be an L/G of 63 gal/Macf and 124,000 gallon reaction tank.

TABLE 2. EFFECT OF PROCESS MAKEUP WATER ON A WESTERN LIMESTONE FGD SYSTEM

| Makeup Water | L/G Ratio (gal/1000 acf) | Reaction Tank Size (1000 gal) | Absorber Feed TDS (1000 ppm) |
|---|---|---|---|
| Untreated Mississippi River water | 63 | 124 | 30 |
| Mississippi River: cooling tower/acid addition | 53 | 124 | 34 |
| Mississippi River: cooling tower/sidestream softening | 14 | 116 | 175 |
| Untreated Lake Sakajawea | 15 | 124 | 74 |
| Lake Sakajawea: cooling tower/acid addition | 12 | 121 | 106 |
| Lake Sakajawea: cooling tower/sidestream softening | 8 | 142 | 216 |

In the western systems, the sludge production rate is only about one-sixth of that in the eastern cases. Since the majority of the water makeup is needed for replacing evaporative losses which are similar for both eastern and western cases, the scrubbing liquors are substantially more concentrated in the western cases due to the lower liquor purge associated with the sludge. Thus, differences in process makeup waters are magnified and the levels of dissolved solids are noticeably higher compared to the eastern coal cases.

Consider, for instance, the change from untreated Mississippi River water (L/G of 63 gal/Macf) to Mississippi River cooling tower blowdown with sidestream softening (L/G of 14 gal/Macf). This is a reduction in L/G of almost 80 percent for the Western case compared to a 40 percent L/G reduction in the eastern case.

Note also that the addition of soda ash in the Lake Sakajawea sidestream softened cooling tower blowdown case does not have as much effect as soda ash addition had in the Mississippi water case. Untreated Lake Sakajawea water is already relatively high in sodium and magnesium so the addition of more sodium has less benefit compared to the Mississippi case.

A caution related to the use of these results should be reiterated. L/G in the 15 to 8 gal/Macf range would not be practical in typical spray tower designs, since mass transfer is generally restricted by liquid-gas surface area limitations. However, the L/G differences show relative effects of the process chemistry and liquid phase alkalinity.

The relative difference in tank size is somewhat higher in the western cases than in the eastern cases with a 20 percent difference between the smallest and largest tanks. The process chemistry which decides the tank size required to prevent scaling is complex with both increases in calcium ion activity and sulfate ion activity across the absorber contributing to the increase in scaling tendency. Changes in concentration of soluble species alters the concentration of the calcium and sulfate ions and the L/G also plays a role in the reaction tank sizing. It should be emphasized that a change in slurry solids concentration of 20 percent (for example from 10 to 12 wt.%) would offset the difference in process chemistry by providing additional gypsum seed crystals for precipitation sites. Thus, differences in process chemistry could be handled in a manner other than increasing reaction tank size.

## EFFECT OF LIME VERSUS LIMESTONE

The eastern coal cases reflect the largest effect of reagent selection as summarized in Table 3. The single most significant effect noted in Table 3 is the difference in reaction tank size between the lime and limestone eastern cases--141,000 gallons and 746,000 gallons, respectively. The smaller tank is a direct result of the assumed sulfite oxidation fraction which is 15 percent for lime compared to 20 percent for limestone. Although many factors influence oxidation, lime systems generally operate with lower sulfite oxidation, probably because of the more reactive reagent. The oxidation levels predicted here allow the lime system to operate subsaturated with respect to gypsum.

Since gypsum scaling is not a problem under the conditions simulated, the lime system reaction tank was sized based on calcium sulfite precipitation and a much smaller tank size was calculated. Differences in oxidation between lime and limestone systems were not assumed for the western cases because the expected oxidation in the western situation is so high that differences in reagent would not be expected to result in subsaturated gypsum operation. Therefore, tank sizes would not change substantially because of the reagent used.

TABLE 3. EFFECT ON LIME VERSUS LIMESTONE FGD SYSTEMS

| | Eastern Coal | | Western Coal | |
|---|---|---|---|---|
| | Lime | Limestone | Lime | Limestone |
| Sulfite Oxidation | 15 | 20 | 90 | 90 |
| Water source | Untreated Mississippi River | Untreated Mississippi River | Untreated Lake Sakajawea | Untreated Lake Sakajawea |
| L/G (gal/1000 acf) | 99 | 133 | 11 | 15 |
| Reaction tank size (1000 gal) | 141 | 746 | 117 | 124 |
| Absorbed feed TDS (1000 gpm) | 20 | 19 | 77 | 74 |

In both the western and eastern cases, the L/G ratios of the lime systems were about 25 percent lower than those of the corresponding limestone systems. Two factors contribute here. First, lime is much more reactive than limestone which tends to lower the required L/G for $SO_2$ removal. Second, the lime selected for study in this project had a slightly higher magnesium-to-calcium ratio than high-calcium quickline and this magnesium provides an additional increase in the liquid phase alkalinity.

## EFFECT OF REAGENT MAGNESIUM CONTENT

The reactive magnesium concentration of the lime or limestone reagent affects the liquid phase alkalinity in a fashion similar to the addition of sodium to the cooling tower blowdown stream which is used as FGD system makeup water. In both cases, the soluble magnesium or sodium content is increased relative to the chloride concentration, and the liquid phase alkalinity increases rapidly as the magnesium and sodium surpass the equivalent chloride content. The effect of magnesium is summarized for eastern and western coal limestone cases in Tables 4 and 5, respectively.

TABLE 4. EFFECT OF REACTIVE MAGNESIUM CONTENT ON AN EASTERN LIMESTONE FGD SYSTEM
Untreated Mississippi River Water

| | Higher Mg Limestone | Lower Mg Limestone |
|---|---|---|
| $MgCO_3$ content (wt%) | 1.5 | 0.15 |
| L/G ratio (gal/1000 acf) | 133 | 234 |
| Reaction tank (1000 gal) | 746 | 765 |
| Absorber feed TDS (1000 ppm) | 19 | 13 |

Table 4 shows that as the reactive magnesium concentration in the limestone increases from a relatively low 0.15 wt.% to 1.5 wt.%, the L/G decreases from 234 to 133 gal/Macf. The liquid phase alkalinity has more than doubled. Note that the low-magnesium system has such poor liquid phase alkalinity that an alternate design would normally be employed rather than designing a single spray tower absorber.

TABLE 5. EFFECT OF REACTIVE MAGNESIUM CONTENT ON AN WESTERN LIMESTONE FGD SYSTEM

Untreated Mississippi River Water

| | Higher Mg Limestone | Lower Mg Limestone |
|---|---|---|
| $MgCO_3$ content (wt%) | 1.5 | 0.15 |
| L/G ratio (gal/1000 acf) | 64 | 66 |
| Reaction tank size (1000 gal) | 124 | 141 |
| Absorber feed TDS (1000 ppm) | 30 | 30 |

The effect of the magnesium content was significantly different for the western cases simulated as shown in Table 5. A tenfold increase in the limestone magnesium content had little effect on the liquid phase alkalinity or L/G in the western case. The difference is that the soluble chloride content in the western FGD liquor is significantly higher than in the eastern system because of the higher degree of liquid concentration experienced in the western systems (same evaporation but lower liquor purge with the sludge). As a result, the magnesium simply displaces calcium from solution with little effect on the concentration of soluble alkaline species. Much of the alkalinity for $SO_2$ sorption comes from solids dissolution in the absorber. If additional magnesium were added, a point would be reached where the equivalent magnesium concentration would exceed the chloride concentration and significant improvements in liquid phase alkalinity would be noted.

## EFFECT OF COAL CHLORIDE CONTENT

A similar effect of magnesium and sodium content relative to chloride was seen in simulations with a higher chloride eastern coal. The effects of tripling the chloride content of the coal on a lime FGD are shown in Table 6.

## TABLE 6. EFFECT OF COAL CHLORIDE CONTENT ON AN EASTERN LIME FGD SYSTEM

Untreated Mississippi River Water/High Magnesium Lime

| | 0.1 Percent Cl Coal | 0.3 Percent Cl Coal |
|---|---|---|
| L/G ratio (gal/1000 acf) | 99 | 249 |
| Reaction tank size (1000 gal) | 141 | 180 |
| Absorber feed TDS (1000 ppm) | 20 | 31 |

The higher coal chloride content increased the chloride concentration of the scrubbing liquor; this chloride displaced alkaline species such as sulfite and carbonate. The increase in chloride decreased the liquid phase alkalinity by a factor of 4. The L/G would be about 250 to achieve 90 percent $SO_2$ removal in a single spray tower. While this design is impractical, the result does emphasize the importance of accounting for the chloride content of the coal.

### Effect of Typical Low Volume Wastewaters

Using low volume demineralizer regeneration and pretreatment softener blowdown wastewater streams had little effect on FGD system operation. The effect of the wastewater addition is small primarily because the flow is less than 3 percent of the total FGD system water makeup rate. If surges were experienced due to variations in wastewater flow rates, the effects could be much more significant.

### Effect of Changing Process Makeup Water Source on an Existing FGD System

A case was simulated to predict the effect that changing the makeup water could have on operation of an existing FGD system. The results are summarized in Table 7.

## TABLE 7. EFFECT OF MAKEUP WATER SOURCE ON OPERATION OF AN EXISTING WESTERN LOW-MAGNESIUM LIMESTONE FGD SYSTEM

| Makeup Water Source | Base Case Untreated Mississippi River | Alternate Water Case Mississippi River/Sidestream Softened Cooling Tower Blowdown |
|---|---|---|
| L/G ratio (gal/1000 acf) | 66 | 66 |
| Reaction tank size (1000 gal) | 141 | 141 |
| $So_2$ removal efficiency (%) | 70 | 98 |
| Gypsum relative saturation | 1.30 | 1.32 |
| Absorber feed TDS (1000 ppm) | 31 | 121 |
| Liquid phase alkalinity (N) | 0.0017 | 0.01 |

The addition of sidestream softened cooling tower blowdown increased the liquid phase alkalinity, resulting in a predicted 98 percent $SO_2$ removal. This assumes that the absorber will not become severely gas-film mass transfer limited, which is a strong possibility. In any case, well above 90 percent removal would occur.

On the negative side, the increased $SO_2$ removal increases the gypsum relative saturation to slightly above the 1.3 scaling threshold which was used as a reaction tank sizing criteria in this study. This is not a major limitation, however, since the suspended solids concentration could be raised slightly to reduce the relative saturation.

## CONCLUSIONS

- Process water selection has a significant effect on the process chemistry. The TDS makeup water is not the major determining factor in evaluating the effect of makeup water on process chemistry. Waters with high $Mg^{++}$ or $Na^{+}$ concentrations relative to $Cl^{-}$ result in higher liquid phase alkalinity and lower L/G.

- Process water selection has an important but less significant effect on the system's scaling tendency than on alkalinity. In most cases, these effects can be compensated for by changing the suspended solids concentration to adjust the seed crystal inventory.

- Other variables such as coal chlorine content and reactive magnesium concentration in the alkaline reagent have an equally important role in determining process chemistry effects.

- In selecting the optimum use for water sources in an FGD system, one must examine the process chemistry effects on specific unit operations such as the mist eliminator or lime slaker, as well as on the main absorber loop.

- Process water selection can affect the optimum FGD system design. Additionally, the feasibility of some designs can be affected by the makeup water used.

# CONTINUOUS EMISSION MONITORING OF FLUE GAS DESULFURIZATION SYSTEMS

by: Peter R. Westlin
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

## ABSTRACT

The Environmental Protection Agency (EPA) has conducted continuous emission monitoring (CEM) studies of varying durations at many flue gas desulfurization (FGD) units. These include eight electric utility size units tested in support of the development of the 1979 new source performance standard (NSPS) (40 CFR Part 60, Subpart Da) for limiting sulfur emissions from electric utilities. Other units include four utility FGD demonstration projects conducted since promulgation of Subpart Da. The EPA has also undertaken a 1-year demonstration of CEM operation on a full-scale FGD system. This CEM system is a complete demonstration of the monitoring requirements of Subpart Da. Further, EPA is revising the evaluation methods and specifications for certifying CEM systems to include knowledge learned in the Agency's and other field test programs.

## INTRODUCTION

On June 11, 1979, EPA published in the Federal Register an NSPS for utility boilers. This NSPS, Subpart Da of 40 CFR Part 60, addresses the emission limits for sulfur dioxide ($SO_2$), oxides of nitrogen ($NO_x$), and particulate emissions from electric utility steam-generating units capable of firing more than 73 MW heat input of fossil fuel. The $SO_2$ emission limit in Subpart Da includes a percentage reduction requirement as well as a limit of $SO_2$ emissions. One result of the promulgation of Subpart Da is the use of flue gas desulfurization (FGD) systems on coal-fired, electric utility boilers. Because the regulation for $SO_2$ emissions requires continuous monitoring of compliance status, CEM upstream and downstream of FGD units has become a major concern of EPA and boiler operators.

EPA has designed, installed, and operated CEM systems on numerous FGD systems since 1977. The experience gained in these projects has led to improvements not only in CEM equipment designs, but also in the procedures used in the operation and evaluation of CEM systems. This increased knowledge is reflected in the development of Subpart Da and the associated test methods, in the revisions of the CEM performance specification and quality assurance (QA) procedures, and in the development of guidelines for CEM installation and operation.

This presentation deals with EPA experiences with installation and operation of CEM systems, a description of the present CEM demonstration project, and the development of revised CEM PS procedures, QA requirements, and guidelines.

## FIELD EXPERIENCE

### SUBPART Da SUPPORT PROGRAMS

The field testing program of FGD emissions and $SO_2$ removal efficiencies began in May 1977. The objective was to collect CEM data for $SO_2$ emission rates and determine removal efficiencies over relatively long periods of time, i.e., 30 days to 6 months. EPA started the field test projects with CEM equipment with which the Agency had become familiar during earlier, studies on units without FGD. In general, the CEM systems have been extractive types of analyzers for the measurement of $SO_2$ and oxygen ($O_2$) concentrations in conditioned stack gas samples. Sample conditioning consisted mainly of primary particulate removal and some moisture removal. The sample probes were equipped with automatic backflushing with high-pressure air to remove particulate and moisture buildup. Sample lines were of heated Teflon tubing designed to avoid moisture and acid condensation. A schematic of this type of CEM system is shown in Figure 1.

Table 1 summarizes the utility boiler and CEM programs conducted by EPA in support of NSPS development. The first eight test programs - Cane Run Number 4, Bruce Mansfield Number 1, Eddystone Number 1, LaCygne Number 1, Shawnee venturi prototype, Lawrence Number 4, Conesville Number 5, and Shawnee turbulent contract absorber prototype - were completed prior to promulgation of Subpart Da. The analyzers for $SO_2$ and $O_2$ used for these projects were generally high quality and performed well in terms of calibration and precision. However, the support equipment including sample probes and lines, sample conditioning units, and data acquisition systems were not state-of-the-art. The Agency encountered numerous problems in operating the total CEM systems on wet FGD units.

Frequent mechanical failures occurred because of the high moisture levels downstream of FGD systems. Probe filters often plugged in spite of backflushing efforts. Cold spots in heated lines filled with condensation and particulate and blocked the lines. In some cases, moisture knock-out traps in front of the analyzers were inadequate for reducing very high moisture levels to acceptable concentrations. In addition, EPA determined that the moisture correction factor for concentrations determined on a wet basis must be based on the moisture level entering the analyzer rather than the stack level. This was because the moisture level was decreased between the stack and the analyzer in the sample conditioning system.

The formidable task of the data recording and data reduction which had not been a major consideration in earlier, short-term single-point measurement programs, became a significant problem in these early FGD studies. In all of these eight programs, the primary methods of data recording were strip chart recorders or paper tape data loggers. All of the data for calculations had to be manually determined from the strip charts including the correlations

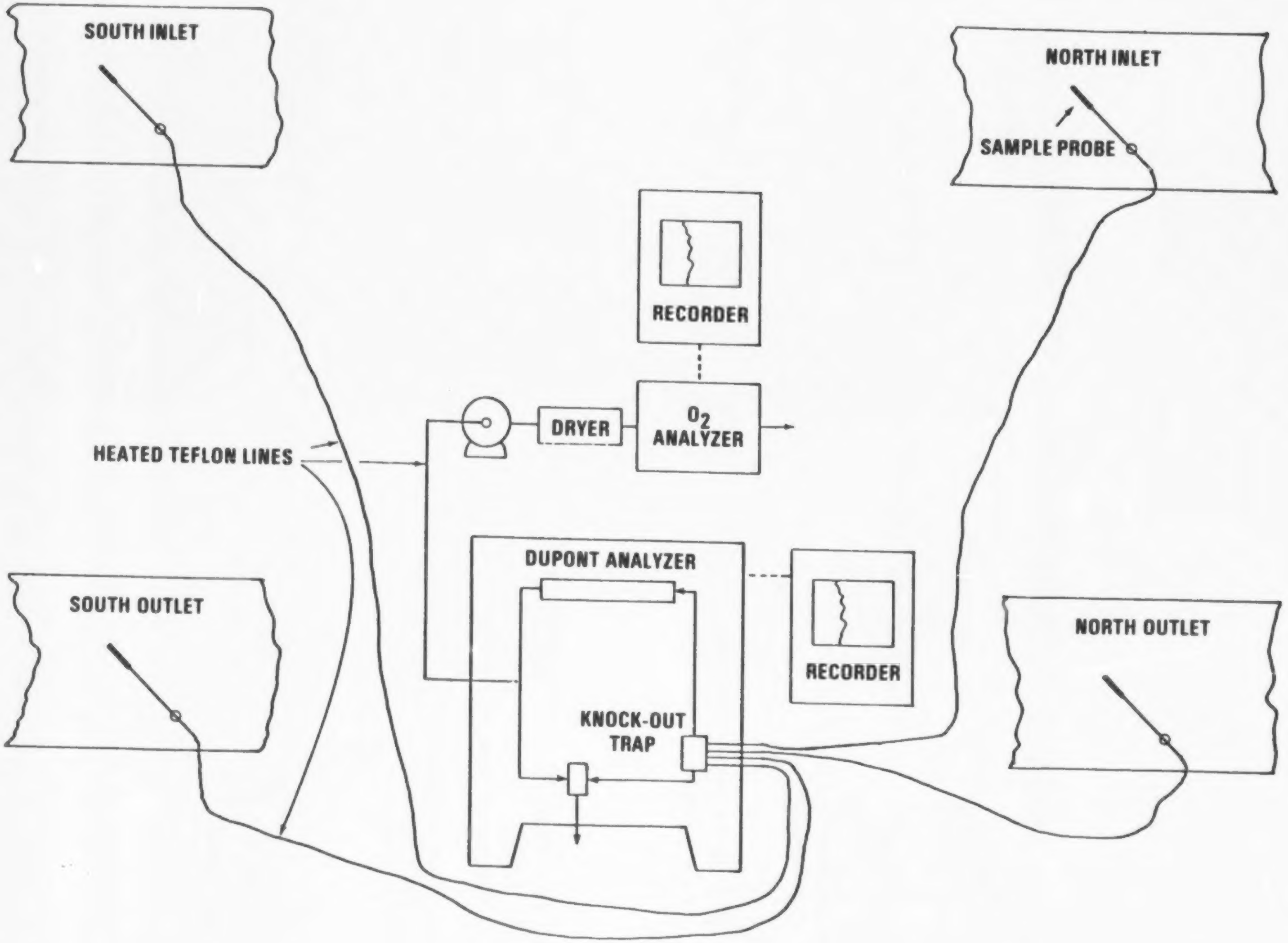


Figure 1. Typical Continuous Emission Monitoring system for early flue gas desulfurization emission studies.

TABLE 1. SUMMARY OF UTILITY STEAM GENERATOR CONTINUOUS EMISSION MONITORING PROGRAMS

| Plant name/location | Type of FGD | CEM description | Number of data days* (initiation date) |
|---|---|---|---|
| 1. Louisville Gas and Electric Company, Cane Run No. 4<br>Louisville, Kentucky | Carbide lime, mobile-bed, spray absorber | $SO_2$ - DuPont** 460 four-point, dual range,<br>$O_2$ - Scott 150 paramagnetic analyzer<br>Data recorder - multi-point | 89 (July 1977) |
| 2. Pennsylvania Power Company's Bruce Mansfield Unit No. 1<br>Pittsburgh, Pennsylvania | Thiosorbic lime, venturi absorber | $SO_2$ - DuPont 460 two-point, inlet, UV analyzer; two DuPont 460 four-point, outlet, UV analyzers<br>$O_2$ - Taylor OA 137 paramagnetic analyzer<br>Data recorder - multi-point, strip chart recorders | 31 (August 1977) |
| 3. Kansas City Power and Light Company, LaCygene, No. 1<br>LaCygne, Kansas | Limestone, venturi absorber | $SO_2$ - DuPont dual range, inlet, UV analyzer; DuPont 460 dual range, two-point, outlet UV analyzer<br>$O_2$ - Not operated successfully<br>Data recorder - multi-point, strip chart recorder | 0 (August 1977) |
| 4. Philadelphia Electric Company, Eddystone Unit No. 1<br>Philadelphia, Pennsylvania | Magnesium oxide, venturi absorber | $SO_2$ - DuPont 460 dual range, five-point, UV analyzer<br>$O_2$ - Manual methods<br>Data recorder - multi-point strip chart recorder | 8 (August 1977) |
| 5. Tennessee Valley Authority Shawnee FGD Prototypes<br>Paducah, Kentucky | Limestone and adipic acid, venturi absorber | $SO_2$ - DuPont 460 UV analyzers at inlet and outlet<br>$O_2$ - Thermox WDG 3, electrocatalytic analyzers<br>Data recorder - four strip chart recorders | 31 (January 1979) |
| 6. Kansas Power and Light Company, Lawrence Unit No. 4<br>Lawrence, Kansas | Limestone bed scrubber/spray tower absorber | $SO_2$ - Thermo electron Model 40 pulsed fluorescence analyzers at inlet and outlet<br>$O_2$ - Beckman Model 742 polarographic, inlet analyzer; MSA model 802 paramagnetic, outlet analyzer<br>Data recorder - multi-point strip chart recorder - and paper tape data logger | 22 (January 1979) |

|  |  |  |  |
|---|---|---|---|
| 7. Columbus and Southern Ohio Electric Company<br>Conesville Unit No. 5<br>Conesville, Ohio | Thiosorbic lime, spherical packing, mobile bed absorber | $SO_2$ - DuPont 460 two-point inlet, UV analyzer; DuPont 460 two-point outlet, UV analyzer<br>$O_2$ - Thermox WDG 3, electrocatalytic analyzers<br>Data recorder - multi-point strip chart recorders | 45 (December 1979) |
| 8. Tennessee Valley Authority<br>Shawnee FGD Prototypes<br>Paducah, Kentucky | Lime, turbulent contact absorber | $SO_2$ - DuPont 460 UV analyzers at inlet and outlet<br>$O_2$ - Thermox WDG 3, electrocatalytic analyzers<br>Data recorder - strip chart recorders | 42 (January 1979) |
| 9. Southern Indiana Gas and Electric Company<br>A.B. Brown Station<br>Evansville, Indiana | Dual alkali scrubber | $SO_2$ - DuPont 400 UV analyzers for inlet and outlet<br>$O_2$ - Thermox WDG 3 for inlet and outlet<br>Data recorder - computer data recorder, CRT terminal, data reduction and printer | 130 (June 1981) |
| 10. Allegheny Power Systems<br>Pleasants Power Station<br>Unit No. 1<br>Willow Island, West Va. | Thiosorbic lime venturi spray absorber - (four modules) | $SO_2$ - DuPont 460 dual range, six-point UV analyzer<br>$O_2$ - Thermox WDG 3 in parallel<br>Data recorder - automatic data acquisition and reduction computer with tape and printer | 268 (June 1981) |
| 11. Springfield City Utilities<br>Southwest Power Plant<br>Springfield, Missouri | Adipic acid enhanced limestone turbulent contact absorber (two modules) | $SO_2$ - DuPont 460 dual range, four-point UV analyzer<br>$O_2$ - Thermox WDG 3 in parallel<br>Data recorder - automatic data acquisition and reduction computer with tape and printer | 400 (January 1981) |
| 12. Louisville Gas and Electric Company, Cane Run No. 6<br>Louisville, Kentucky | Dual alkali spray absorber | $SO_2$ - DuPont 460 two-point UV analyzer at inlet Lear Siegler SM-810 in-situ at outlet<br>$O_2$ - Hagen/Westinghouse in-situ electrocatalytic analyzer at inlet Lear Siegler CM-50 at outlet<br>Data recorder - Lear Siegler DP-30 data acquisition and reduction for outlet data<br>Automatic Data System (ADS) for all data, including inlet. | 150 (July 1980) |

*Data day is defined as 24-hour period of boiler operation (12:01 a.m. to midnight) during which 75 percent of the CEM data were collected.

**Mention of a specific company or product name does not constitute endorsement by the U.S. Environmental Protection Agency.

of FGD inlet and outlet data, pollutant and diluent values, emissions and process data, and any calibration changes. These data then had to be input into a computer program for final reduction to emission rates and percent reduction values. The time consumed in completing the data reduction rivaled the length of the field tests themselves.

## ADDITIONAL FGD EVALUATION STUDIES

Four FGD studies were undertaken in 1980 and 1981 by EPA with view toward evaluating improvements in FGD designs and operation. A summary of these four programs - A.B. Brown, Pleasants Number 1, Southwest Power, and Cane Run Number 6 - is also shown on Table 1. EPA conducted CEM studies at four industrial boilers equipped with FGD systems, as well. A discussion of the industrial boiler studies is not included here.

Several improvements based on the experience of earlier studies were incorporated into the CEM systems. Among the improvements was the use of very high pressure (>70 psi) air in backflushing sample lines and probes. Increased air pressure improved the removal of particulate and moisture from the probes and filters in the stack both upstream and downstream of the FGD units. Because primary filters were frequently plugged and corroded in earlier applications, in-stack filters were redesigned with better shields or other protection or were removed completely for these later programs. Removal of the in-stack filter required that sample conditioning outside the stack be upgraded to ensure the analyzers were protected from particulate and moisture. Heated coarse filters and improved moisture removal devices were used successfully.

The development of computers to handle data acquisition and data reduction for CEM measurements was a significant improvement. A considerable amount of time spent at the initiation of these programs in developing computer programs to accept the raw outputs from the CEM systems, correlate the pollutant and diluent data, make necessary moisture and temperature corrections, calculate emission rates and percent reduction rates, and record all the data in a usable format. The data handling systems could also produce acceptable report summaries as well as calculate running hourly, daily, or other period averages. The quick availability of emission data allowed EPA to evaluate the process variables continually and to make adjustments to FGD operations without delays for manual data reduction procedures. The time spent in developing the computer programs and the data acquisition systems was returned several times over in the increased availability of reduced and usable data. Figure 2 shows a schematic of a CEM system typical of those used in these four studies.

## THE CEM DEMONSTRATION PROJECT

The promulgation of Subpart Da emphasized the role of CEM systems by requiring continuous compliance with emission standards. In addition to emission measurements of $SO_2$ and $NO_x$, Subpart Da required an $SO_2$ reduction determination. This provision doubles the $SO_2$ monitoring requirements for FGD units and requires additional data reduction steps.

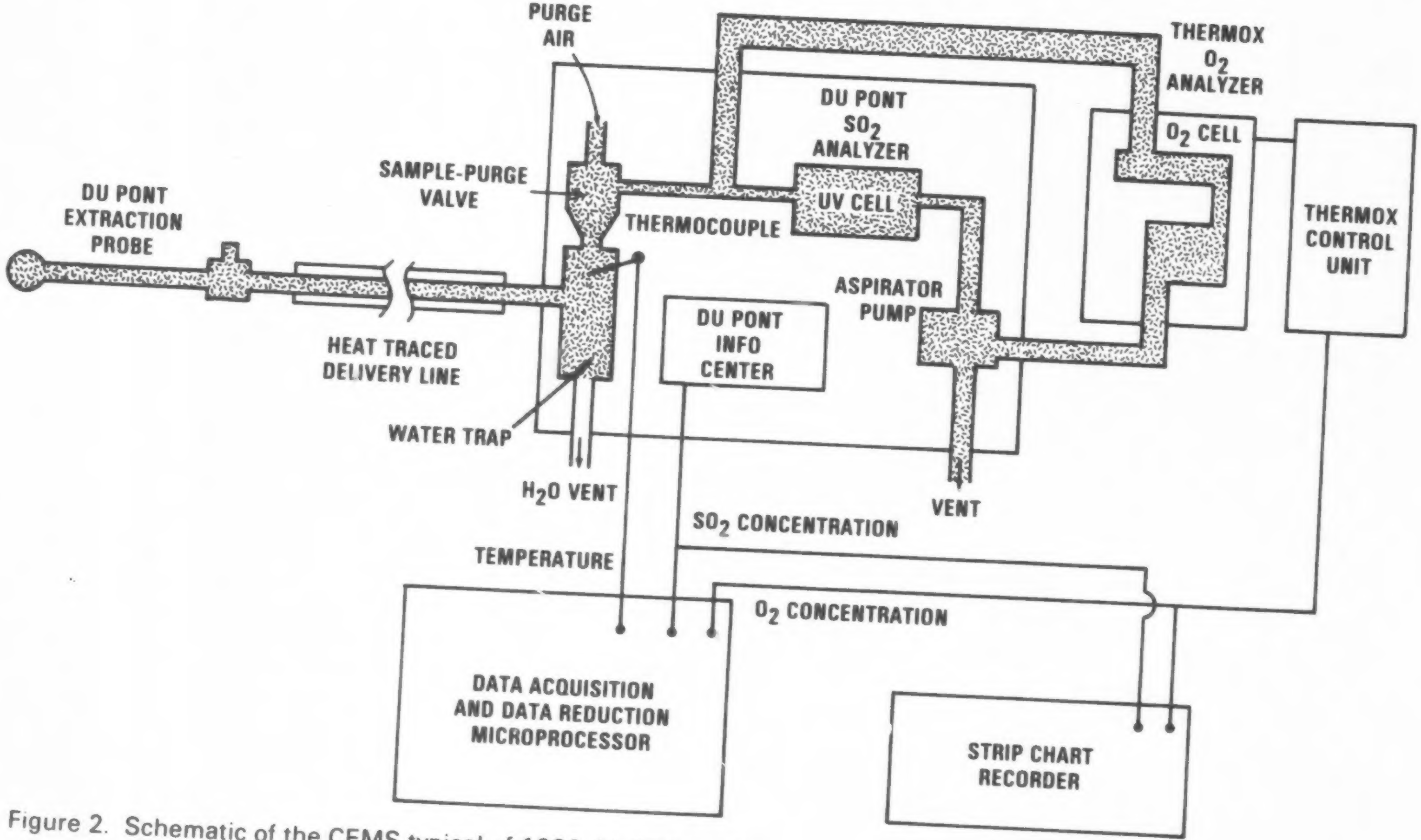


Figure 2. Schematic of the CEMS typical of 1980-81 FGD studies.

EPA undertook in late 1979, to demonstrate the feasibility of the CEM requirements of Subpart Da through a field test project. The CEM systems used in earlier studies had not been designed for long-term operation as would be the case for a source required to meet Subpart Da. By operating a CEM system for a year, EPA could also collect background support data for QA requirements that will become part of 40 CFR Part 60.

EPA selected Columbus and Southern Ohio Electric Company's (now American Electric Power Company) Conesville Number 6 unit for the field demonstration. Figure 3 shows both Conesville Numbers 5 and 6. Unit 6 has a rated capacity of 411 MWE and combusts bituminous coal with a sulfur content of 4.7 percent, an ash content of 15 to 17 percent, and a heating value of about 10,000 Btu/lb. This sulfur content is equivalent to about 8 lb/MM Btu (3500 ng/J) at the inlet to the FGD unit. Particulate matter is controlled by two, parallel module, cold-sided, electrostatic precipitators. The exhaust gases flow from the precipitator to a UOP Air Correction Division, wet thiosorbic lime scrubber. The scrubber is a turbulent contact absorber designed to treat the total boiler effluent; however, some of the flue gas is by-passed under normal operation for reheat purposes. Gases from the FGD modules and the by-pass duct are combined in a common duct and emitted through an 800-foot stack.

Monitoring probe points are located at each scrubber module inlet and at the combined exhaust duct upstream of the stack entrance. The CEM system consists of $SO_2$ and $O_2$ monitors at the inlet locations and $SO_2$, $NO_x$, and $O_2$ measurements at the exhaust site. The CEM system, shown schematically in Figure 4, was specified by EPA's contractor, GCA Technology Division, and designed and constructed by KVB, Inc.

The FGD inlet monitoring unit is a DuPont 400, two-point uv analyzer in parallel with a Thermox WDG 3 electrocatalytic $O_2$ analyzer. This measurement system operates on a time-sharing basis between the two inlet sample points. The outlet gas is monitored by a similar DuPont/Thermox unit operated on a smaller $SO_2$ concentration scale with capabilities to increase the scale automatically if the gas concentration exceeds the span of the instrument. The $NO_x$, also monitored at the outlet location, is analyzed with a Thermo Electron Model 10A chemiluminescent analyzer. Gas samples are drawn from each of the three locations through stainless steel probes. A coarse, in-stack sintered steel filter is used on the inlet; no in-stack filter is used on the outlet probes. A glass fiber mat filter is contained outside the stack in a heated, sample conditioning and valve-switching box.

The CEM system is designed to operate automatically. A computer controls the daily drift determinations, the multipoint calibrations, data acquisition and storage, and data reporting. The CEM system has the capability of communicating with the operator remotely through a modem telephone line connection. An on-site terminal allows the operator to recall any data, modify the program, or activate any portion of the CEM functions as necessary. A backup, strip-chart recorder is connected directly to the analyzers.

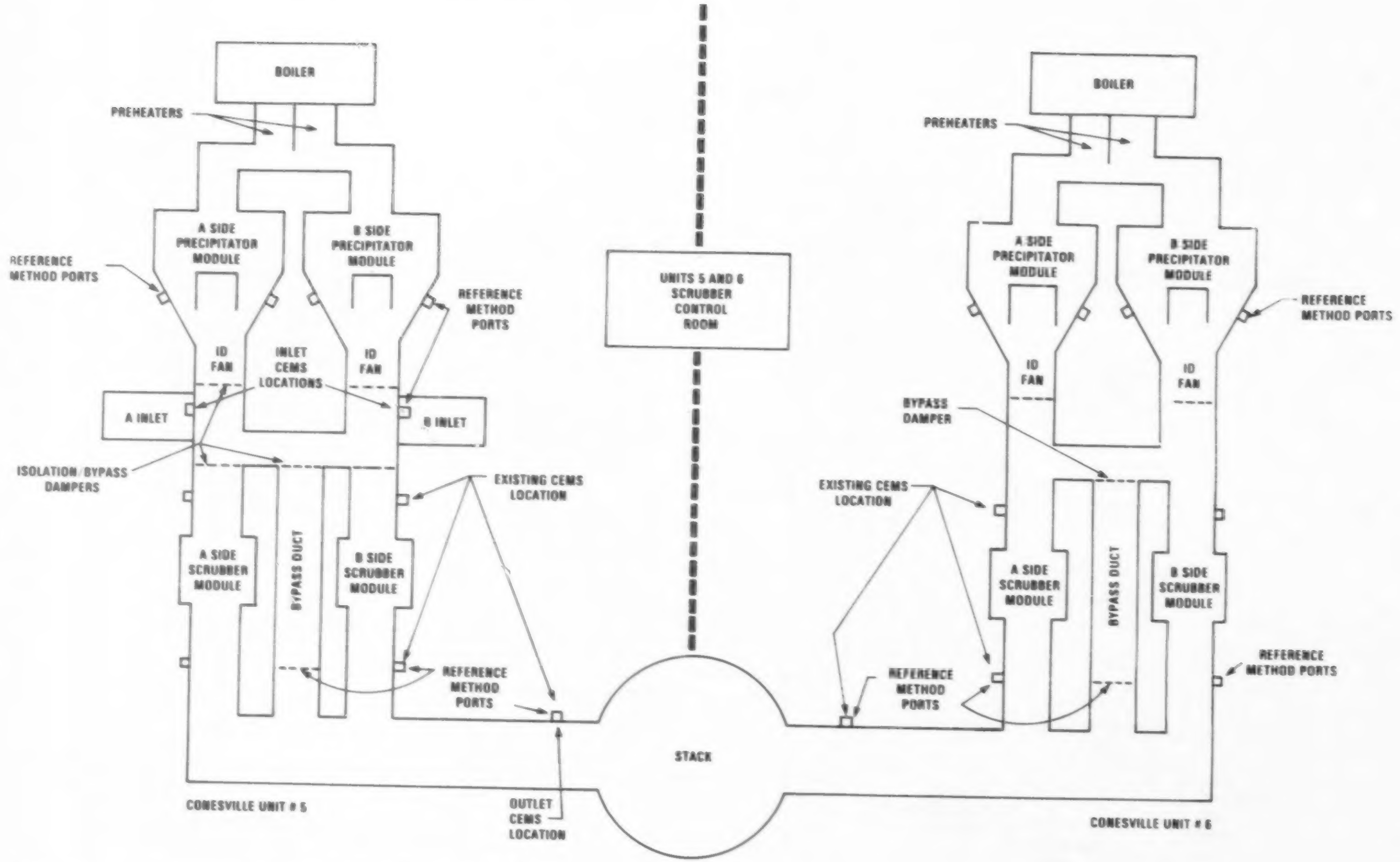


Figure 3. Conesville Units 5 and 6

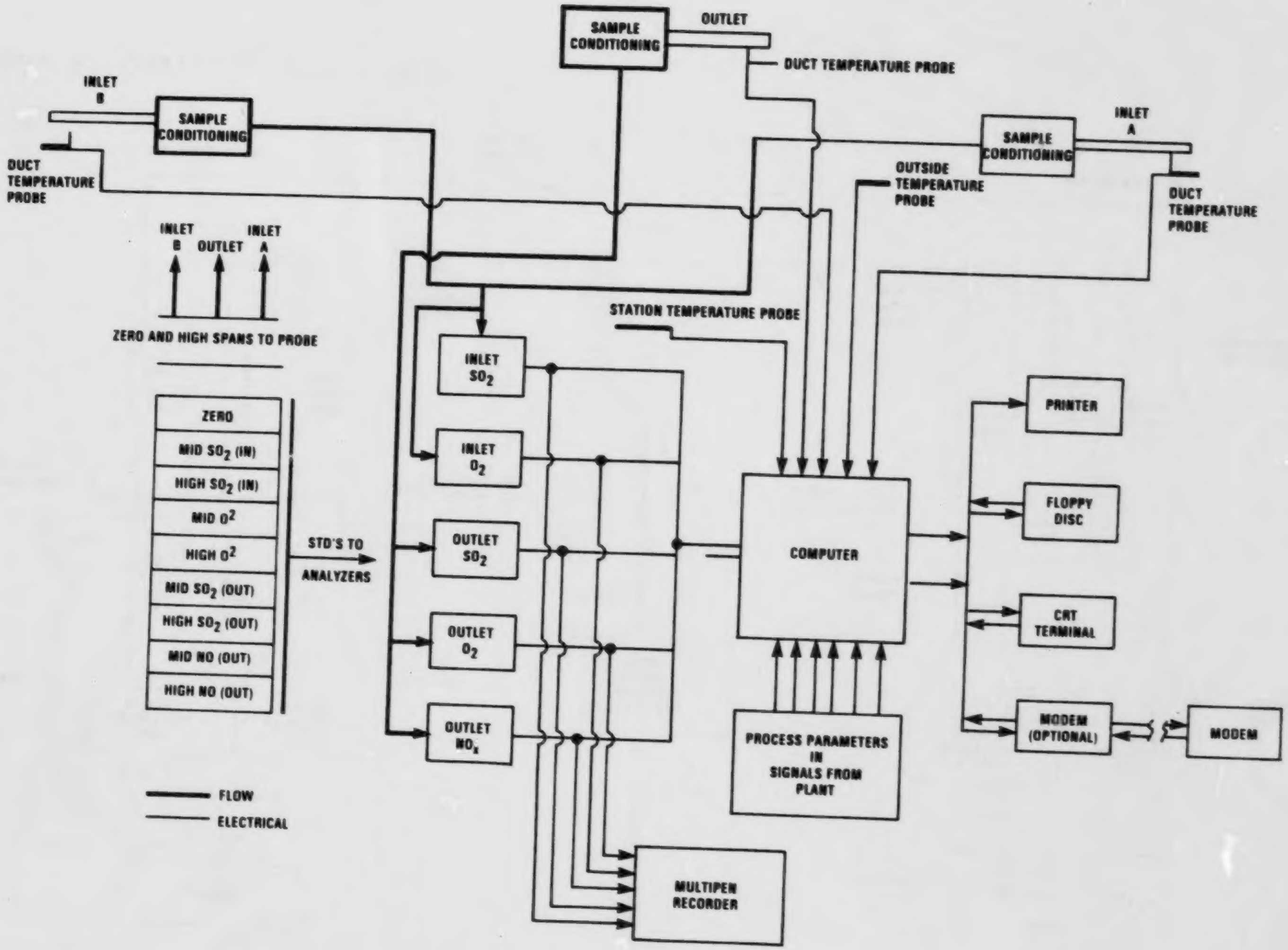


Figure 4. Conesville Number 6 CEM System Block Diagram

The CEM system was installed and operating by June 1981. Certification tests, including stratification checks, were completed according to the procedures in Performance Specifications (PS's) 2 and 3 of Appendix B, 40 CFR Part 60. All of the CEM system parameters were checked against criteria set forth in the PS. These parameters include instrument drift, calibration error, response time, and relative accuracy (RA). The CEM system was subject to the RA tests as a system; that is, the RA was determined not only for the individual analyzer responses (e.g., $SO_2$ concentration in ppm), but also for the CEM system in units of the emission standard (e.g., $SO_2$ emission rate in lb/MM Btu). This RA test checked not only the pollutant analyzer, but also the diluent analyzer and the computer system.

Startup problems included sample line leakages, electrical grounding problems (common at an electric utility plant), computer software problems, and mechanical pump and switching failures. These problems can be considered common occurrences for new CEM systems. About 3 months was required to install the CEM and correct these problems prior to the PS test period.

The test contractor is conducting periodic abbreviated QA and RA tests in order to assess the continued operability of the CEM. The results of the initial PS tests and the first abbreviated RA test are shown on Table 2.

Following the initial period of equipment shakedown and computer program corrections, the CEM system has operated with very low manual attention and high reliability. The preventive maintenance program and the nonroutine maintenance requirements have averaged less than 15 hours per week. The CEM availability has been over 85 percent for the period since the initial PS test.

EPA intends to operate the CEM system at Conesville Number 6 for 1 year. This period was chosen as the minimum duration that would adquately demonstrate the long-term capabilities of a state-of-the-art CEM system.

## PERFORMANCE SPECIFICATIONS AND QUALITY ASSURANCE

### PERFORMANCE SPECIFICATIONS 2 AND 3

With the increased emphasis on CEM for compliance monitoring, the EPA undertook a review of the CEM PS with a view toward modification. The EPA published in the Federal Register in October 1979, proposed revisions to PS 2 and 3. These revisions were essentially restatement of the promulgated versions with expanded sections on installation, calibration procedures, and alternative procedures for various types of CEM systems. This proposal brought numerous comments from CEM users, manufacturers, and regulators. The comments have caused the EPA to review the goals of the PS and to define the important, critical criteria by which CEM should be evaluated.

This review led to reproposal of PS's 2 and 3 in the Federal Register on January 26, 1981. These latest PS provide only two criteria for evaluating CEM. These are RA and instrument drift. The RA is a measure of the ability of the CEM system to measure the pollutant emission rate compared to measurements with EPA reference methods. Instrument drift is a measure of

TABLE 2. CONESVILLE PERFORMANCE DATA SUMMARY

| | Inlet A | | Inlet B | | Outlet | | |
|---|---|---|---|---|---|---|---|
| | DuPont $SO_2$ | Thermox $O_2$ | DuPont $SO_2$ | Thermox $O_2$ | DuPont $SO_2$ | Thermox $O_2$ | TECO $NO_x$ |
| 2- hour drift | | | | | | | |
| zero | 0.1% FS | 0.01% $O_2$ | 0.38% FS | 0.10% $O_2$ | 1.04% FS | 0.17% $O_2$ | 0.68% FS |
| Cal | 0.7% FS | 0.05% $O_2$ | 0.89% FS | 0.18% $O_2$ | 2.00% FS | 0.23% $O_2$ | 0.93% FS |
| 24- hour drift | | | | | | | |
| Zero | 0.3% FS | 0.07% $O_2$ | 0.78% FS | 0.15% $O_2$ | 3.2% FS* | 0.17% $O_2$ | 0.77% FS |
| Cal | 2.5% FS | 0.28% $O_2$ | 1.7% FS | 0.65% $O_2$ | 6.4% FS* | 0.22% $O_2$ | 1.6% FS |
| Calibration error | | | | | | | |
| Mid | 1.4% | 1.7% | 0.95% | 1.5% | 6.7%* | 0.8% | 2.3% |
| High | 0.5% | 1.1% | 0.57% | 0.9% | 1.6% | 2.5% | 1.2% |

| Relative accuracy | DuPont $SO_2$ | Thermox $O_2$ | DuPont | Thermox | TECO |
|---|---|---|---|---|---|
| Analyzers | 4.3% | 0.4% $O_2$ | 11.0% | 0.3% $O_2$ | 12.8% |
| System | 6.5% | | 15.6% | 15.2% | |
| Abbreviated relative accuracy Test No. 1 | | | | | |
| Analyzer | 11.5% | 0.5% ($O_2$) | 15.8% | 0.4% ($O_2$) | 6.7% |
| System | 14.9% | | 16.8% | 9.7% | |

*Failed the specifications initially. An autozero system has been installed and the CEM now meets all

FS = Full scale.

the CEM system measurement stability over a specific period time. The EPA feels that a CEM system that demonstrates compliance with strict specifications for these two criteria is performing adequately. Much of the basis for this conviction is a result of the experience gained from the FGD studies discussed earlier.

The promulgation package for PS 2 and 3 is now being put in final form. The promulgated version will be much like the January 1981 proposal and will apply to all new or modified CEM systems. Publication is expected within the next few months.

## CEM GUIDELINES

Many users and operators of CEM systems have used the 1975 PS not only for certification tests, but also for guidance in the installation and preparation of CEM equipment. EPA feels that so many different types of instruments and installation sites are encountered that PS that included all the options and alternatives would be awkward and confusing as a regulation. As stated above, EPA feels that only two criteria are necessary for evaluating CEM operations. However, EPA recognizes that much of the experience gained by the Agency would be valuable to others who need to install and operate CEM systems. For this reason, a document entitled "Gaseous Continuous Emission Monitoring System Specification Guidelines," has been made available from the Emission Standards and Engineering Division, Mail Drop 19, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

The purpose of the guideline is to provide a supplement to proposed PS 2 and 3. The document includes guidelines for installation and suggested test procedures and data reduction procedures for evaluating the capabilities of gaseous CEM systems. These guidelines do not provide procedures for long-term evaluation of CEM systems or assessing data quality beyond the initial performance test. The guidelines recommend that the operator develop procedures for long-term QA evaluations in accordance with the CEM manufacturer recommendations and the applicable regulation.

## THE QA REQUIREMENTS

The EPA recognizes the need to provide QA procedures especially for CEM used to provide compliance data. The QA Division of the Office of Research and Development is developing an appendix for 40 CFR Part 60 that would address QA in general and a section specifically for compliance CEM. The procedures in this appendix would be mandatory for compliance testing and will become part of the regulatory procedures.

The CEM QA, soon to be proposed, describes: (1) criteria for CEM corrective actions based on span drift data; (2) criteria for CEM data invalidation; and (3) procedures for assessing the accuracy and precision of CEM data. Quarterly audits will be proposed to assess CEM data accuracy. The quarterly audit may be performed by a relative accuracy audit (RAA), a cylinder gas audit (CGA), or an EPA approved alternative. The RAA is based on six RA tests rather than nine as specified in PS 2. If the CGA is selected, it must be alternated every other quarter with the RAA. Precision is calculated on a monthly basis using daily span drift checks currently required by the regulations.

## CONCLUSIONS

EPA has gained a considerable amount of experience in the installation and operation of CEM systems on utility boilers with FGD systems. These test programs have helped not only in the collection of $SO_2$ emission and reduction data, but also in the development and improvement in the operation of CEM equipment. These improvements have become increasingly important as CEM is recognized as the primary means of assessing the performance of FGD systems.

Many technical problems have been encountered in the application of CEM. These include: conditioning of wet, particulate-laden samples for instrument analysis; measurement of highly variable pollutant and diluent concentrations; coordination of multiple-point sample collection and analyses; and reducing great quantities of data into understandable summaries. The CEM equipment used by EPA and industry has developed from basic analyzer and recorder systems with little sophistication and numerous mechanical problems into computer operated, automatic systems with high availability and lower maintenance requirements.

Capital costs for CEM systems have increased substantially from the first installations. These increases are due to vital improvements in the sample handling and conditioning equipment and to the increased use of computers and automatic operation. The benefits obtained through the increased capital costs are a decrease in operation and maintenance costs and an increase in CEM system availability. Whereas early CEM systems often required 24-hour operator attendance and many hours of manual data reduction, state-of-the-art systems require less than 2 days per week of manual attention and can be programmed to produce written, complete reports. In addition, availability of CEM systems has increased from less than 50 percent in the earliest programs to over 85 percent for a CEM system meeting all the measurement requirements of Subpart Da.

## BIBLIOGRAPHY

1. Kelly, W.E., et al. Air Pollution Emission Test Report. First Interim Report: Continuous Sulfur Dioxide Monitoring at Steam Generators. Emission Measurement Branch. Report No. 77SPP23A. Office of Air Quality and Standards. U.S. Environmental Protection Agency. August 1979.

2. Kelly, W.E., et al. Air Pollution Emission Test. Second Interim Report: Continuous Sulfur Dioxide Monitoring at Steam Generators. Emission Measurement Branch. Report No. 77SPP23B. Office of Air Quality Planning and Standards. U.S. Environmental Protection Agency. March 1979.

3. Kelly, W.E., et al. Air Pollution Emission Test. Third Interim Report: Continuous Sulfur Dioxide Monitoring at Steam Generators. Emission

Measurement Branch. Report No. 77SPP23C. Office of Air Quality Planning and Standards. U.S. Environmental Protection Agency. March 1979.

4. Peduto, E.F. and G. Quackenbos. CEMS Design for the 1-Year Continuous Monitoring Demonstration Program. GCA Report 1146. Prepared for U.S. Environmental Protection Agency. Industrial Environmental Research Laboratory. Research Triangle Park, N.C. April 1980.

5. Peduto, E.F., T.J. Porter, and D. Harris. Operational Experience With Two Continuous Emission Monitoring Systems on Coal-Fired Power Plants. APCA Specialty Conference. November 1981.

6. Peduto, E.F., R.B. Strong, and W.B. Kuykendal. Continuous Monitoring for Sulfur Dioxide at a Utility Boiler Equipped with a Limestone Scrubber. APCA Journal, Vol. 31, No. 2. February 1981.

7. Sedman, C.B. Sulfuric Dioxide Emission Data for an Industrial Boiler New Source Performance Standard. Proceedings: Symposium of Flue Gas Desulfurization. Volume 2. October 1980.

8. Proposed Performance Specification 2. Specifications and Test Procedures for $SO_2$ and $NO_x$ Continuous Emission Monitoring Systems in Stationary Sources. Federal Register (46 FR 8342). January 26, 1981.

# FULL-SCALE UTILITY FLUE GAS DESULFURIZATION SYSTEM CHARACTERIZATION RESULTS

by: Richard G. Rhudy
Electric Power Research Institute
Palo Alto, CA

Wayne E. Morgan, Ph.D.
Earl O. Smith, P. E.
Black & Veatch Consulting Engineers
Kansas City, MO

Philip S. Lowell, Ph.D., P. E.
P. S. Lowell & Company, Inc.
Austin, TX

## ABSTRACT

The Electric Power Research Institute (EPRI) initiated a full-scale flue gas desulfurization characterization project to provide data which will assist electric utilities in optimizing the operation of existing wet scrubber systems, aid in the selection of new scrubbing systems, and provide informed responses to possible new emission requirements. The project is directed at performing extensive and detailed evaluations of the emission control capabilities of selected, representative, currently operating, full-scale wet scrubbing systems. The scrubber systems that have been characterized are Columbus and Southern Ohio Electric Company's Conesville Unit 5 and Montana Power Company's Colstrip Unit 2.

The selected scrubber systems were characterized by field testing and engineering analysis. Measurements were performed for currently regulated emissions as well as several unregulated emissions in the gas, liquid, and solid streams of the scrubber systems. Sulfur dioxide, nitrogen oxides, particulate, fine particulate, trace elements, particulate size-segregated trace element distributions, sulfuric acid mist, chlorides, fluorides, organics, carbon dioxide, and carbon monoxide were measured in scrubber influent and effluent streams. In addition, mist eliminator performance, scrubber generated particulate, and scrubber sludge measurements were performed. These measurements, combined with scrubber process chemistry information, operating data, and design characteristics, provide a detailed understanding of the performance of the scrubber systems. Material balances and other techniques for establishing data consistency and reasonableness were applied in an effort to identify the limitations and quality of the data collected. Areas where potential improvements in scrubber operations could be made are identified.

## INTRODUCTION

The electric utility industry is making a large and growing commitment to lime and limestone wet scrubbing for sulfur dioxide ($SO_2$) emission control on coal fueled power plants. The utilities operating these systems, however, typically do not have the resources to optimize system operation with respect to operating costs, nor do most utilities have the time to perform detailed comparisons of their systems with current state of the art technology to aid them in selecting systems for future installations. Lack of this information can result in higher than necessary operating costs on existing systems and higher than necessary capital costs on new systems.

At the same time the utilities are trying to operate existing scrubbing systems, new governmental regulations are being proposed and implemented that may have a major impact on the design and, in some cases, possible use of these systems. Stricter sulfur dioxide ($SO_2$) emission limitations were recently implemented as part of the June 1979 revised New Source Performance Standards (NSPS), and new limitations are being considered for currently unregulated discharges such as fine particles, organic materials, volatile metals, and trace elements. Existing data on the magnitude of these discharges and the effects of existing flue gas cleaning equipment on them are limited.

The Electric Power Research Institute (EPRI) initiated the "Full-Scale Scrubber Characterizations" project to provide data which will assist electric utilities in optimizing the performance of their existing flue gas desulfurization systems, aid them in selecting new systems, and provide informed responses to possible new emission requirements. This program is thus designed to characterize the overall performance of representative utility wet-scrubber systems.

## CHARACTERIZATION PROGRAM APPROACH

Regulated and currently unregulated scrubber emissions data were collected from selected utility scrubber systems along with process chemistry information, and then combined with operating data and scrubber design characteristics to provide a detailed understanding of the influence that a scrubber system has on the flue gas. Representative full-scale wet scrubber systems were selected for the present characterization program based on availability and compatibility with desired design and operating experience criteria. Following selection of the systems, site surveys were conducted to identify existing and potential sampling locations, determine plant modifications required to support testing activities, and establish available variations in operating parameters and testing conditions. Installed instrumentation was calibrated, and the plant was modified to facilitate sampling, including installation of additional flow monitoring equipment, connections, and test support facilities. Field data and samples were collected and analyzed for several different test conditions. Where possible, scrubber system performance was evaluated as a function of process variations, including variations of boiler load and scrubber operating conditions, such as scrubber pH and liquid-to-gas ratio. The field sampling results, operating history data, scrubber design characteristics, and capital and operating cost data were then evaluated. The evaluations were directed at determining the significance of the results, the quality of the data, and the areas where potential improvements might be made in scrubber operations. A summary of the categories of data collected as part of the EPRI scrubber characterization program is presented below.

Regulated Emissions

- Sulfur Dioxide ($SO_2$)
- Nitrogen Oxides ($NO_x$)
- Total Particulate

Unregulated Emissions

- Fine Particulate Matter (size distribution and penetration data over a nominal size range of 0.02 to 20 micrometers)
- Trace Elements (overall elemental distribution in all scrubber inlet and outlet streams as well as size-segregated fine particle distribution and penetration across the scrubber)
- Organic Materials
- Sulfuric Acid ($SO_3$)
- Chlorides (HCl) and Fluorides (HF)
- Carbon Monoxide (CO) and Carbon Dioxide ($CO_2$)

System Operational Characteristics

- Scrubber Process Chemistry
- Scrubber Generated Particulate
- Mist Eliminator Performance (droplet entrainment and removal)
- Scrubber Sludge
- Historical Scrubber Operating Data

Engineering and Economic Evaluation

- Detailed System Description
- Operational Problems and Solutions
- Reliability and Availability
- System Costs

## SCRUBBER SYSTEMS SELECTED FOR CHARACTERIZATION

The scrubber systems selected for characterization were Columbus and Southern Ohio Electric Company's Conesville Unit 5 and Montana Power Company's Colstrip Unit 2.

### Conesville Unit 5

Conesville Unit 5 is a 411 megawatt power plant which began operation in January 1977 and burns high-sulfur eastern coal. The air quality control system for this unit consists of an electrostatic precipitator (ESP), followed by a flue gas desulfurization (FGD) system. The cold-side ESP is designed to remove 99.65 per cent of the particulate to comply with the applicable federal NSPS of 0.1 lb/MBtu of heat input. The FGD system is designed to remove a minimum of 90 per cent of the $SO_2$ and meet a state $SO_2$ emission limit of 1.0 lb/MBtu of heat input which is more restrictive than the applicable NSPS of 1.2 lb/MBtu.

A simplified single-module diagram of the Conesville Unit 5 scrubber system is shown on Figure 1. Each of the two turbulent contact absorber (TCA) scrubber modules on Unit 5 is designed to treat approximately 60 per cent of the flue gas flow. The TCA absorber modules, provided by Universal Oil Products Air Correction Division, are rubber-lined carbon steel vessels containing one level (6 to 8 inches) of mobile spheres (1.5 inches in diameter) to provide a turbulent contacting area for $SO_2$ removal. Lime, containing about 3 to 5 per cent magnesium, is the $SO_2$ removal additive. Following treatment by the absorbers, the gas passes through a trap-out tray and two banks of horizontal, chevron-type mist eliminators. Full flue gas bypass capability permits operation to continue when the FGD system is down for maintenance.

The slurry bleed stream from the recycle tank is sent to a thickener. The thickener is designed to settle the slurry to an underflow solids content of about 30 per cent. Thickener overflow is recycled to the scrubbing system and the underflow is pumped to a sludge fixation facility where it is further dewatered by a vacuum filter. A pug mill mixes the sludge with lime and dry fly ash. The system is designed to produce a solid waste containing 50 to 60 per cent solids. A conveyor and radial stacker place the mixture into a diked sludge disposal area located on the site.

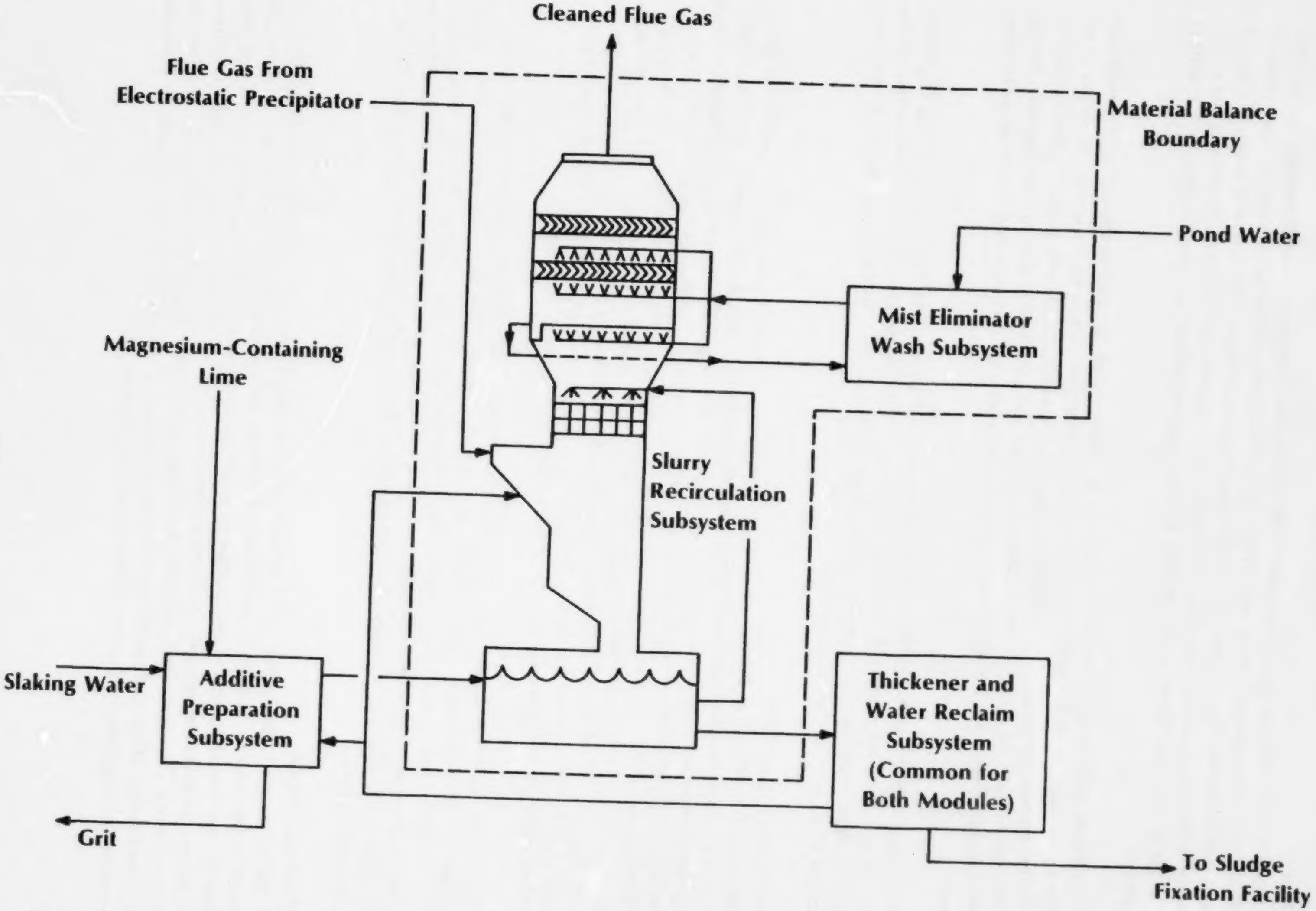

Cleaned Flue Gas
Flue Gas From Electrostatic Precipitator
Material Balance Boundary
Pond Water
Mist Eliminator Wash Subsystem
Magnesium-Containing Lime
Slurry Recirculation Subsystem
Slaking Water
Additive Preparation Subsystem
Thickener and Water Reclaim Subsystem (Common for Both Modules)
Grit
To Sludge Fixation Facility

Figure 1. Simplified Conesville Unit 5 (Module 5B) FGD System Diagram

### Colstrip Unit 2

Colstrip Unit 2 is a 358 megawatt low-sulfur western coal fueled power plant which initiated operation in July 1976. The Colstrip Unit 2 air quality control system consists of a variable-throat venturi/spray tower scrubber which removes both particulate and $SO_2$. A simplified single-module diagram of the scrubber system is shown on Figure 2. The scrubber is designed to comply with state and federal particulate emission limits of 0.10 lb/MBtu and a stack opacity of 20 per cent. The system is also designed to meet state and federal $SO_2$ emission limits of 1.2 lb/MBtu of heat input.

Unit 2 is served by three scrubber modules with no flue gas bypass capability. Each scrubber module was designed to handle a maximum of 40 per cent of the flue gas for a limited time if maintenance is required on one of the modules. The scrubber was supplied by Combustion Equipment Associates. After exiting the $SO_2$ absorber portion of the scrubber module, the flue gas passes through a wash tray and a single-stage chevron mist eliminator. The gas exits the scrubber module and passes through a reheat section consisting of two banks of in-line plate-coil steam reheaters.

The slurry bleed from the scrubber consists of a mixture of gypsum scrubber reaction products ($CaSO_4 \cdot 2H_2O$) and fly ash. The scrubber solids mixture is pumped into a permanent disposal pond located on the Colstrip site near the FGD system. Water from the disposal pond is returned to the FGD system. The system operates closed loop with no discharge of water other than by evaporation.

## SAMPLING AND ANALYSIS

The test program conducted at Conesville Unit 5 and Colstrip Unit 2 involved field sampling of all gaseous, liquid, slurry, and solid scrubber inlet and outlet streams as summarized on Figure 3. The sampling and analyses were made to characterize emissions and scrubber process chemistry and to perform material balances around a selected representative single scrubber module for major and trace species as shown on Figures 1 and 2. Sampling was performed during several different combinations of boiler and scrubber system operating conditions during two separate test series conducted at Conesville and during a single test series at Colstrip. Each sampling period was preceded by a period of selected scrubber and boiler operating conditions which was long enough for the system to stabilize and approach a steady state period for testing. The controlled operating and sampling conditions were established to assure that the results would be representative of the scrubber operating conditions tested.

Scrubber system performance was evaluated for regulated emissions including sulfur dioxide, nitrogen dioxide, and particulate. Unregulated emissions were characterized including size-segregated particulate and trace element distribution and penetration, overall trace elements, organic materials, sulfuric acid, chlorides, fluorides, carbon monoxide, and carbon dioxide. Scrubber system operating characteristics were established by performing process chemistry measurements, characterizing scrubber generated particulate and mist eliminator performance, and collecting historical operating data.

## DATA EVALUATION

The Conesville Unit 5 and Colstrip Unit 2 scrubber field test performance data, operating experience information, scrubber design features, and actual system cost information were all examined in detail to provide an integrated evaluation and characterization of the scrubber systems. Scrubber module material balances and other data quality checks were performed to establish the reasonableness, accuracy, and limitations of the data collected. Scrubber emission levels and removals were determined for a wide range of both regulated and unregulated emissions. However, the emphasis of the study is on $SO_2$ removal, the purpose of the scrubber system, including an examination of exactly how $SO_2$ is removed by the scrubber systems characterized.

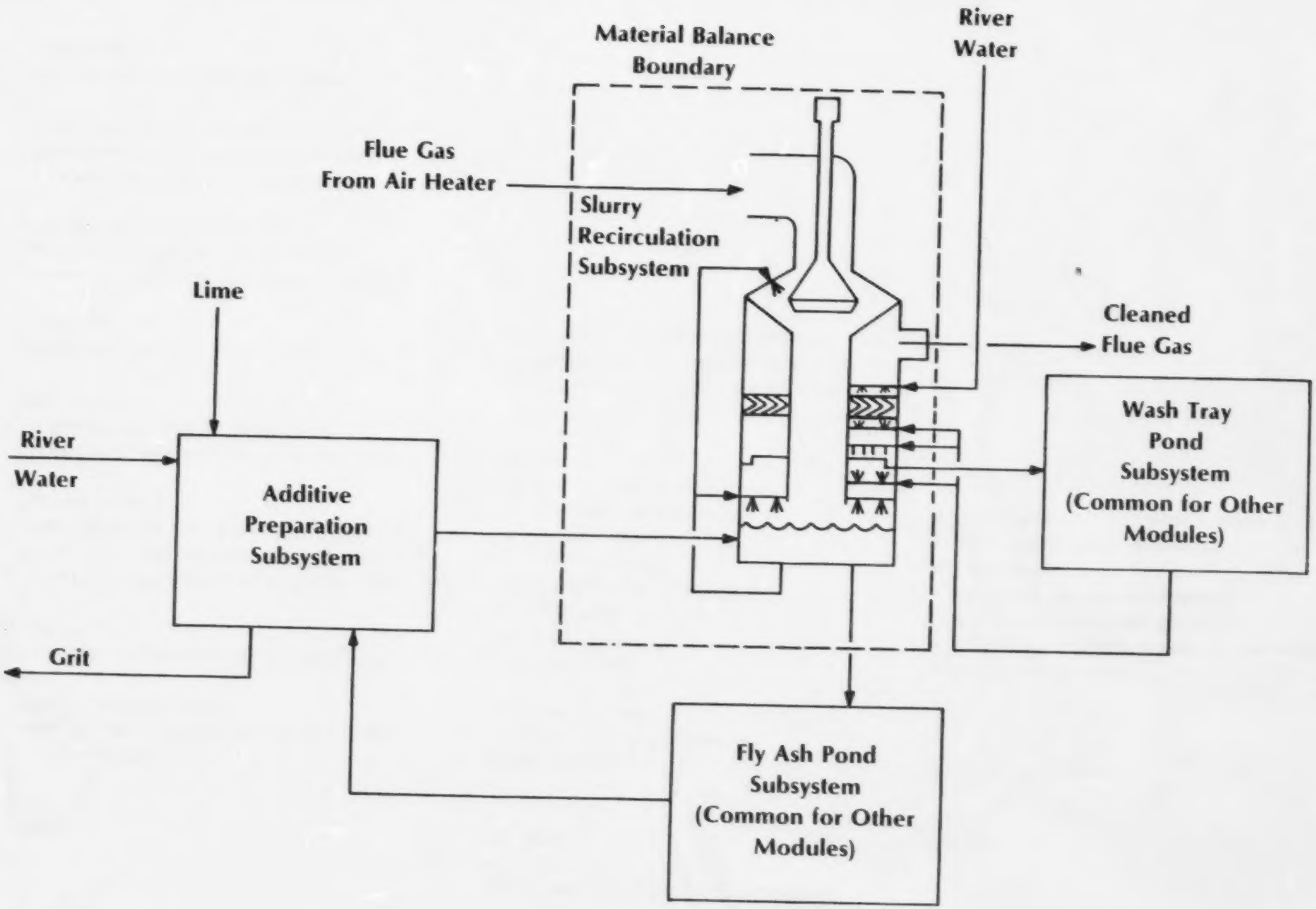


Figure 2. Simplified Colstrip Unit 2 (Module 2A) FGD System Diagram

SAMPLING AND ANALYSIS PROGRAM

**GAS**

- Continuous Monitors ($SO_2$, $O_2$, $NO_x$, CO, $CO_2$ at Inlet and Outlet of the Scrubber Module)
- Controlled Condensation System ($SO_3$, HCl, and HF)
- University of Washington Impactors (Inlet and Outlet of Scrubber Module for Particle Size Distribution and Trace Element Concentration by Particle Size)
- Electrical Aerosol Analyzer (Inlet and Outlet of Scrubber Module for Particle Size Distribution)
- Droplet Photography (Mist Eliminator Performance)
- Source Assessment Sampling System (Inlet and Outlet of the Scrubber Module for Organics and Trace Elements)
- EPA Method 5 (Inlet of each Scrubber Module and Outlet of Module or at the Stack to Determine Total Mass Loading)
- On-Line Gas Chromatography (Volatile Hydrocarbons)

**LIQUID**

Grab Samples
(Rapid Filtration Required for Selected Samples)

- Service Water
- Lime Slurry
- Pond Water Overflow
- Mist Eliminator Wash Water
- Recycle Slurry
- Absorber Outlet Flow
- Absorber Slurry Drawoff
- Wash Tray Pond Return
- Pond Return

(Anion/Cation Analysis, Organic Analysis, Total Suspended Solids, Total Dissolved Solids, Density, pH, Solids Quality, Acid Insolubles, Particle Size Distribution)

**SOLIDS**

Composite Grab Samples

- Coal (Trace Elements)
- Bottom Ash (Trace Elements and Organics)
- Economizer Ash (Trace Elements)
- Air Heater Ash (Trace Elements)
- Precipitator Ash (Trace Elements)
- Lime (Cation/Anion Analysis)
- Slaker Rejects, "Grit" (Acid Insolubles)

Figure 3. Full-Scale Scrubber Characterization Sampling and Analysis Program

## RESULTS

Scrubber characterization test results are presented below for the Conesville Unit 5 scrubber, followed by a parallel discussion of the Colstrip Unit 2 scrubber. Most of the program results are presented in abbreviated form in this paper. Selected results judged to be of general interest are discussed in additional detail.

### CONESVILLE UNIT 5

#### Test Conditions

The variations in test conditions achieved were a combination of those selected and those dictated by operational constraints. Variables selected for investigation included boiler load, flue gas flow, and liquid-to-gas (L/G) ratio. Significant variations resulting from scrubber operational changes were also experienced for pH and additive (lime) reagent ratio (the molar ratio of calcium and magnesium added, to sulfur removed). The Conesville test conditions are summarized in Table 1.

Testing was conducted over a range of boiler load conditions from 60 to 100 per cent, with 1 or 2 modules in service, to vary the gas flow to each module so that significant changes in the emissions due to differences in load would be characterized. However, because of variations in excess combustion air, flue gas bypass, and scrubber modules in operation, a relatively small variation in flue gas flow to test Module 5B was experienced. The scrubber recycle slurry flow was varied during the tests to establish a range of L/G ratios from about 35 to 70 gallons/$10^3$ acf. Variations in recycle flow were accomplished by increasing or decreasing the number of recycle pumps in operation from two to four (three is typical). Additive reagent ratio varied from about 1.0 to 1.3. The scrubber slurry operating pH varied over a range of about 6.0 to 7.5.

#### Regulated Emission Characterization

**Sulfur Dioxide ($SO_2$)** – Average $SO_2$ removals for all tests ranged from 95.3 to 99.2 per cent as summarized in Table 2. Generally, as shown on Figure 4, the higher removals corresponded to higher L/G ratios. However, the $SO_2$ removal range was considered too narrow and too near 100 per cent to establish a quantitative relationship. The pH and reagent ratio were also important in $SO_2$ removal as evidenced by differences in test results from the first (Tests 1 through 4) and second (Tests 5 through 7) test series. An estimated 1 to 2 per cent $SO_2$ removal occurs in the presaturator section based on calculations performed. Nearly all of the $SO_2$ removal occurs in the absorber section. A more detailed discussion of why this system is capable of very high $SO_2$ removal is provided subsequently as part of the scrubber process chemistry section.

An average $SO_2$ emission rate for Module 5B of 0.062 lb/$10^6$ Btu was measured for the first test series and 0.27 lb/$10^6$ Btu for the second series. It should be noted that the emission rates quoted are for a single module only. The $SO_2$ removal provided by the second module and the amount of flue gas bypass determine overall unit emission rates. Also, the $SO_2$ data for each test are taken over about a one day controlled period and would not necessarily reflect long-term control and operation of the module. The $SO_2$ removal values do suggest that the system is chemically capable of $SO_2$ removals in excess of 90 per cent.

**Particulate** – The scrubber generally provided some additional particulate removal efficiency (10 to 90 per cent) as measured by EPA Method 5 (the reference method for particulate measurements). However, one set of measurements indicated a higher concentration of particulate at the outlet than at the inlet (–40 per cent collection efficiency).

Because the Conesville scrubbers are preceded by a high efficiency electrostatic precipitator, sampling emphasis was not originally placed on the scrubber particulate removal except with regard to scrubber-generated-particulate. However, difficulties were experienced in collecting mass loading and size distribution data. The problem was attributable to the presence of sulfuric acid condensing across the scrubber.

## Table 1. Summary of Test Conditions for Conesville Unit 5

| System Conditions | | | | | Scrubber Module 5B | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Flue Gas at Scrubber Inlet | | | | | | | | | | | | | | | | |
| Test(a) | Boiler Load | | Modules In Service | Bypass(b) | Flow Rate | | Temperature | | $H_2O$ | $O_2$ | $CO_2$ | Excess Air(c) | Scrubber ΔP(d) | | Liquid Rate | | Recycle Pumps | L/G Ratio(e) | | Recycle Slurry pH | Molar(f) Reagent Ratio |
| | MW | (%) | | % | $m^3/s$ | (kacfm) | C | (F) | % | % | % | % | kPa | (in. wg.) | m/s | (gpm) | | $\frac{m^3}{km^3}$ | $\left(\frac{gal}{kacf}\right)$ | | |
| 1 | 325 | (79) | B | 38 | 375 | (790)(g) | 136 | (276) | 8.4 | 5.9 | 12.0 | 37.0 | 1.09 | (4.4) | 1.95 | (31,000) | 3 | 5.2 | (39.2) | 7.5 | – – |
| 2 | 321 | (78) | A&B | 16 | 275 | (580) | 125 | (257) | 5.3 | 6.2 | 12.3 | 40.6 | 1.34 | (5.4) | 2.32 | (36,800) | 4 | 9.4 | (70.5) | 7.7 | 0.93 |
| 3 | 400 | (98) | B | 59 | 307 | (650) | 125 | (257) | 6.4 | 5.8 | 12.5 | 36.6 | 1.39 | (5.6) | 1.91 | (30,000) | 3 | 6.9 | (51.6) | 6.7 | 1.35 |
| 4 | 400 | (98) | B | 58 | 304 | (640) | 122 | (252) | 5.7 | 5.4 | 13.2 | 33.1 | 1.49 | (6.0) | 2.26 | (35,900) | 4 | 8.2 | (61.0) | 7.0 | 1.23 |
| 5 | 325 | (79) | A&B | 12 | 285 | (600) | 127 | (259) | 6.6 | 7.2 | 11.0 | 50.7 | 1.24 | (5.0) | 1.70 | (27,000) | 3 | 6.8 | (50.6) | 6.1 | 1.02 |
| 6 | 240 | (58) | B | 47 | 292 | (620) | 140 | (284) | 5.7 | 9.2 | 10.8 | 76.5 | 1.27 | (5.1) | 1.76 | (27,900) | 3 | 7.2 | (53.5) | 6.1 | 1.08 |
| 7 | 321 | (78) | A&B | 17 | 282 | (600) | 130 | (267) | 6.2 | 8.1 | 12.3 | 62.2 | 1.17 | (4.7) | 1.21 | (19,200) | 2 | 5.0 | (37.4) | 6.4 | 1.10 |

(a) Tests 1 through 4 are the first test series and 5 through 7 are the second test series.

(b) Bypass amount is estimated using predicted boiler gas flow adjusted for excess air differences and the flow rate for Module A, which is based on pressure loss and L/G ratio using design curves.

(c) Based on Module 5B measured $O_2$.

(d) Includes mist eliminator.

(e) Liquid-to-gas (L/G) ratio calculated using measured liquid rate and saturated gas flow rate at scrubber conditions.

(f) Overall reagent ratio based on moles of calcium and magnesium added to sulfur removed (estimated error is ±0.14).

(g) Measured flow rate based on partial traverse of duct (this test only).

TABLE 2. FLUE GAS SULFUR DIOXIDE ($SO_2$) CONCENTRATIONS AND SCRUBBER REMOVAL EFFICIENCY FOR CONESVILLE MODULE 5B[a]

| Test | Inlet ppm | Inlet ng/J | Inlet (lb/$10^6$ Btu) | Outlet ppm | Outlet ng/J | Outlet (lb/$10^6$ Btu) | $SO_2$ Removal[b] (per cent) |
|---|---|---|---|---|---|---|---|
| 1 | 2,370 | 2,200 | (5.12) | 19 | 18 | (0.041) | 99.2 |
| 2 | 2,220 | 2,110 | (4.92) | 23 | 22 | (0.051) | 99.0 |
| 3 | 2,430 | 2,330 | (5.41) | 46 | 45 | (0.10) | 98.1 |
| 4 | 2,380 | 2,220 | (5.17) | 18 | 17 | (0.040) | 99.2 |
| 5 | 2,710 | 2,950 | (6.86) | 79 | 88 | (0.20) | 97.1 |
| 6 | 2,800 | 3,490 | (8.11) | 80 | 100 | (0.23) | 97.2 |
| 7 | 3,060 | 3,490 | (8.11) | 142 | 164 | (0.28) | 95.3 |

[a] Values in parts per million by volume from continuous monitor data on a dry basis and averaged over the test period for Module 5B only. Values on a weight per fuel value basis were calculated by using a factor representing a ratio of the volume of dry flue gas generated to the calorific value of the fuel burned (EPA "F" factor method). This factor was then adjusted to the actual excess air present in the flue gas as determined by the oxygen content.

[b] Based on lb/$10^6$ Btu values.

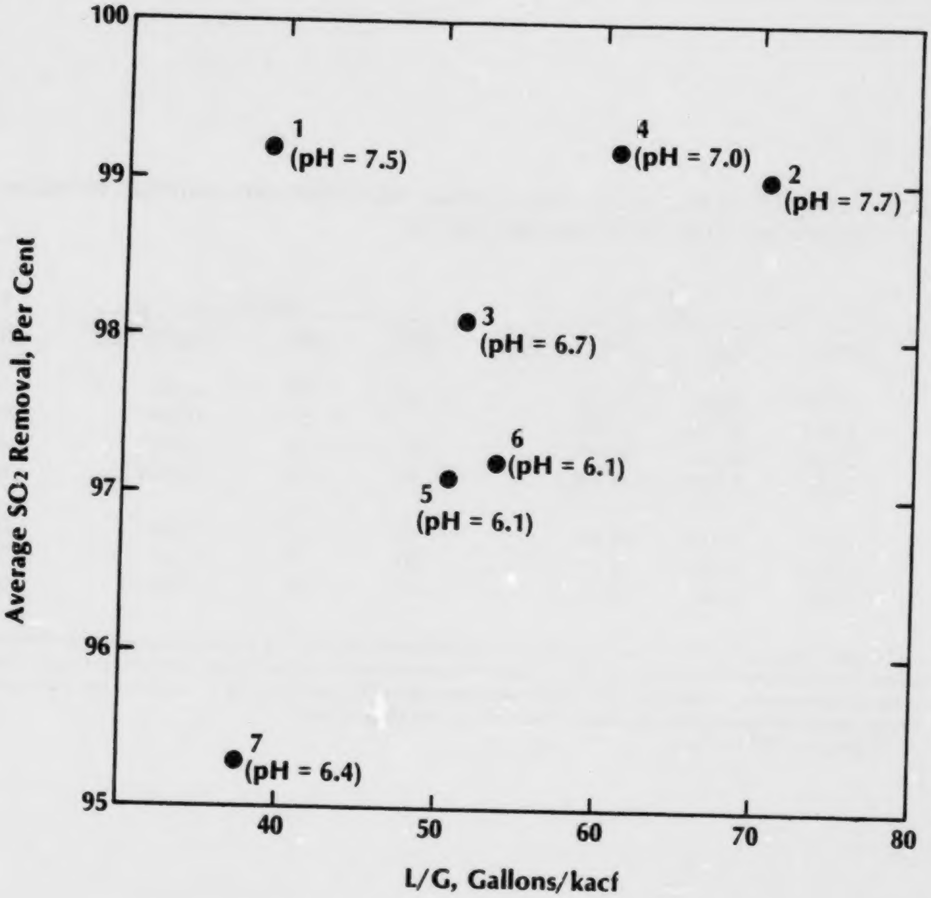


Figure 4. Average $SO_2$ Removal as a Function of Liquid-to-Gas (L/G) Ratio for Conesville Scrubber Module 5B. Test Numbers and Average Scrubber Recycle Slurry pH Values are Indicated for the First (Tests 1-4) and Second (Tests 5-7) Test Series.

The standard method for collecting particulate mass loading data, EPA Method 5, designates 250 F as the collection temperature. This value is below the acid condensation point for Conesville and thus condensed acid is captured as mass emissions at the scrubber outlet. The EPA Source Assessment Sampling System (SASS) train used for particulate, trace element, and organic materials sample collection was operated at 350 F and did not collect the acid. Mass loading values for the SASS train were about one order of magnitude lower than the EPA Method 5 values. The sulfuric acid values, when converted to corresponding mass loadings, accounted for most of the observed differences. Elemental analysis also indicated that the mass collected was dominated by the presence of sulfur. The mass loading results are summarized in Table 3. Because of the presence of the condensing acid, the scrubber particulate collection efficiency results should be used carefully. At present, since the EPA has not established a particulate matter reference method that does not experience sulfuric acid mist interference problems, particulate matter emissions may be sampled prior to a wet flue gas desulfurization system to demonstrate compliance.

**Nitrogen Oxides ($NO_x$)** – The scrubber is ineffective for the removal of $NO_x$; typically most cases showed only a slight reduction of less than 5 per cent. An average module emission rate of 0.55 lb/$10^6$ Btu was measured over the entire test series.

**Unregulated Emissions Characterization**

**Fine Particulate** – Particle size distributions were measured at the inlet and outlet of the scrubber using impactors and an electrostatic aerosol size analyzer (EASA). Condensed sulfuric acid captured on the impactor collection plates appeared to react with the substrates and casts doubt on the validity of the impactor results. The EASA results indicated a strong mass peak around 0.1 to 0.2 micrometers which is believed to be condensing sulfuric acid. Figure 5 presents the EASA particle size distribution data for the scrubber inlet, outlet, and penetration (outlet/inlet). The presence of condensing acid is consistent with the high penetration values observed.

**Trace Elements** – Trace elements entering and leaving the scrubber were measured by elemental analysis of samples collected from the scrubber module inlet and outlet gas, liquid, slurry, and solids streams. Flue gas trace element measurements are presented in Table 4. Overall, the scrubber provided some removal of trace elements usually considered nonvolatile. These elements, which exhibited removals over a broad range from about 0 to 90 per cent efficiency, included Al, Ba, Be, Cd, Co, Fe, K, Mn, P, Sr, V, and Zr.

In many cases, the scrubber also reduced the concentration of elements considered volatile. Removals for the elements As, Cr, Hg, Ni, and Zn ranged from 31 to 97 per cent. Removals for Se, however, were always negative, and two of the three measurements for Pb indicated negative removals. Three of the five measurements for Zn and two of the five measurements for As indicated negative removals. As shown in Table 4, several nonvolatile elements also had negative removals for some of the measurements. Elements in this category included Ca, Cu, Mg, Mo, Na, and Ti.

The information in Table 4 shows that elemental concentrations varied up to two orders of magnitude for a given element at a given location. Possible reasons for this large variation include (1) nonrepresentative sample, (2) sample inhomogeneity, (3) actual variation, (4) analytical error, and (5) slurry entrainment at the scrubber outlet. Until reliable techniques are developed which can quantify or eliminate these possible errors, conclusions based on this type of data remain uncertain.

The data taken for elemental penetration (scrubber outlet/inlet concentration) as a function of particle size indicated that many elements were penetrating in the 0.1 to 1.0 micrometer diameter size. However, the impactors used to obtain the samples for these data also indicated a very low mass loading; therefore the samples may not be representative. Most of the scrubber outlet appeared to be sulfur which suggests that condensed sulfuric acid caused most of the mass penetration in this size range.

## TABLE 3. FLUE GAS PARTICULATE CONCENTRATIONS AND COLLECTION EFFICIENCY FOR CONESVILLE UNIT 5 SCRUBBER[a]

| Test | Scrubber Module | Inlet | | | | Outlet | | | | Collection Efficiency[b] (per cent) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | mg/Nm$^3$ | (gr/dscf) | ng/J | (lb/10$^6$ Btu) | mg/Nm$^3$ | (gr/dscf) | ng/J | (lb/10$^6$ Btu) | |
| 2 | 5A | 185 | (0.081) | 71.9 | (0.167) | 165 | (0.072) | 64.4 | (0.150) | 10.2 |
| | 5B | 195 | (0.085) | 68.2 | (0.159) | 167 | (0.073) | 59.1 | (0.137) | 13.8 |
| 3 | 5A | 389 | (0.170) | 167 | (0.389) | 119 | (0.052) | 51.1 | (0.119) | 69.4 |
| | 5B | 316 | (0.138) | 124 | (0.289) | 20.6 | (0.009) | 8.1 | (0.019) | 93.4 |
| 5 | 5B | 135 | (0.059) | 56.1 | (0.131) | 82.4 | (0.079) | 34.0 | (0.079) | 39.7 |
| 7 | 5B | 144 | (0.063) | 59.2 | (0.138) | 195 | (0.085) | 81.9 | (0.191) | -38.4 |

[a] Concentrations are based on EPA Method 5, sampling over a two to three hour period. Values in milligrams per dry normal cubic meter and grains per dry standard cubic foot are given at 20 C (68 F) and 760 mm Hg (29.92 in Hg). Values on a weight per fuel value basis were calculated by using a factor representing a ratio of the volume of dry flue gas generated to the calorific value of the fuel burned (EPA "F" factor). This factor was then adjusted to the actual excess air present in the flue gas as determined by the oxygen content.

[b] Based on lb/10$^6$ Btu values.

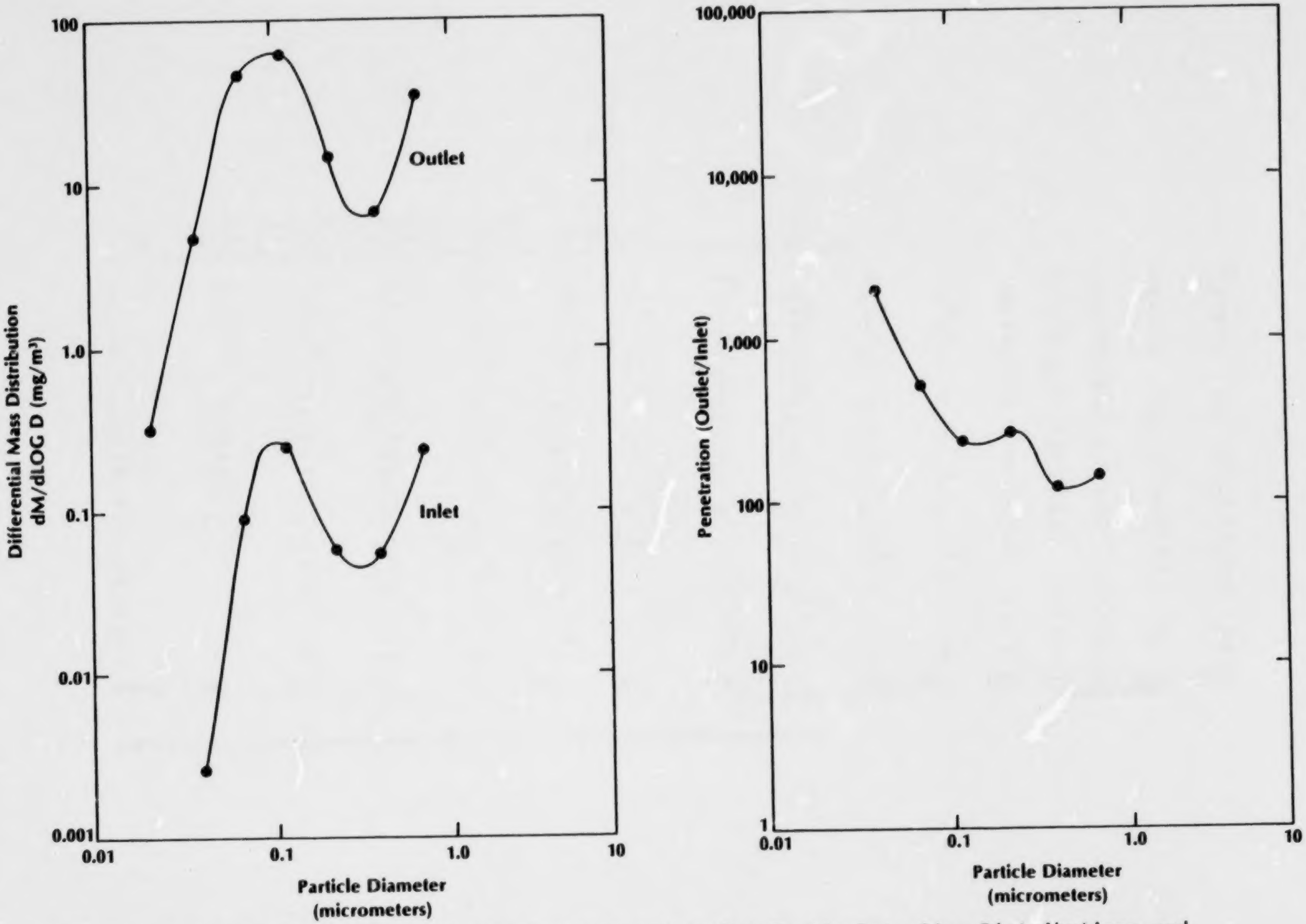


Figure 5. Conesville Scrubber Module 5B Inlet and Outlet Particulate Size Distributions and Penetration (Outlet/Inlet) Measured with an Electrical Aerosol Size Analyzer.

## TABLE 4. FLUE GAS TRACE ELEMENT CONCENTRATIONS FOR CONESVILLE SCRUBBER MODULE 5B[a]

| Element[b] | Inlet, microgram/m$^3$ | | | | | Outlet, microgram/m$^3$ | | | | | Removal, per cent | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Test 2 | Test 3 | Test 4 | Test 5 | Test 7 | Test 2 | Test 3 | Test 4 | Test 5 | Test 7 | Test 2 | Test 3 | Test 4 | Test 5 | Test 7 |
| Al | 210 | 620 | 690 | 90 | 41 | 27 | 230 | 99 | 61 | 29 | 87 | 63 | 86 | 32 | 29 |
| As | 5.4 | 14 | 14 | 4.0 | 2.9 | 3.1 | 3.9 | 5.2 | 14 | 11 | 42 | 72 | 63 | -250 | -276 |
| Ba | 20 | 17 | 11 | c | c | 1.2 | 2.8 | 3.2 | c | c | 93 | 83 | 70 | – | – |
| Be | 0.005 | 0.074 | 0.034 | 0.010 | c | 0.0040 | 0.019 | 0.0070 | c | c | 20 | 74 | 79 | – | – |
| Ca | 1,500 | 730 | 4,700 | 140 | 45 | 430 | 2,500 | 1,400 | 540 | 12 | 71 | -239 | 69 | -288 | 73 |
| Cd | c | c | c | 9.0 | 47 | c | c | c | 4.0 | 38 | – | – | – | 56 | 19 |
| Co | 36 | 44 | 79 | 1.5 | 0.6 | 9.3 | c | c | 0.70 | 0.80 | 74 | – | – | 58 | 0.0 |
| Cr | 3,200 | 3,700 | 7,900 | 2,400 | 2,900 | 1,000 | 470 | 490 | 71 | 360 | 68 | 87 | 94 | 97 | 88 |
| Cu | 0.85 | 22 | 30 | 23 | 13 | 17 | 3.3 | 4.7 | 27 | 23 | −1,935 | 86 | 84 | −18 | −74 |
| Fe | 13,000 | 17,000 | 42,000 | 11,000 | 13,000 | 4,500 | 1,700 | 2,100 | 380 | 1,600 | 67 | 90 | 95 | 97 | 88 |
| Hg | 5.5 | 8.6 | 9.4 | 9.2 | 9.6 | 0.67 | 3.3 | 2.3 | 1.5 | 1.7 | 88 | 31 | 75 | 84 | 82 |
| K | 8.2 | 88 | 45 | 10 | 20 | c | 16 | c | 10 | 9.0 | – | 82 | – | 0.0 | 55 |
| Mg | 260 | 64 | 640 | 8 | 13 | 87 | 340 | 210 | 98 | 17 | 67 | −429 | 67 | −1,125 | −29 |
| Mn | 340 | 420 | 710 | 220 | 280 | 97 | 42 | 49 | 13 | 47 | 71 | 90 | 93 | 94 | 83 |
| Mo | 300 | 360 | 520 | 4.9 | c | 110 | 86 | 600 | 2.7 | 48 | 62 | 76 | −16 | 45 | – |
| Na | 760 | 310 | 2,900 | 19 | 30 | c | 1,000 | 260 | 420 | 120 | – | −241 | 91 | −2,095 | −303 |
| Ni | 2,300 | 2,900 | 4,100 | 740 | 890 | 740 | 400 | 760 | 56 | 360 | 68 | 86 | 82 | 92 | 59 |
| P | 1.7 | 16 | 8.1 | c | c | 1.0 | 6.9 | 2.9 | c | c | 41 | 57 | 64 | – | – |
| Pb | 110 | 56 | 260 | c | c | 61 | 250 | 350 | c | c | 43 | −341 | −36 | – | – |
| Se | 18 | 39 | 41 | 0.20 | 6.4 | 46 | 50 | 54 | 17 | 52 | −153 | −26 | −32 | −8,550 | −708 |
| Sr | 1.8 | 3.4 | 3.4 | 1.0 | 0.60 | 0.12 | 1.7 | 0.17 | 0.70 | 0.30 | 93 | 52 | 95 | 30 | 50 |
| Ti | 7.1 | 32 | 17 | 13 | 11 | 1.1 | 8.4 | 2.0 | 19 | 18 | 85 | 74 | 88 | −52 | −58 |
| V | 7.0 | 9.4 | 16 | 5.4 | 7.1 | 4.9 | 2.2 | 0.22 | 0.20 | 0.80 | 31 | 77 | 99 | 96 | 89 |
| Zn | 40 | 22 | 14 | 27 | 4.3 | 18 | 11 | 120 | 34 | 58 | 55 | 51 | −743 | −26 | −1,249 |
| Zr | 7.3 | 4.8 | 8.9 | 0.30 | 0.10 | c | 0.25 | c | 0.1 | 0.1 | – | 95 | – | 67 | 0.0 |

[a] All concentrations are normalized to 20 C (68 F) and 760 mm Hg (29.92 inches Hg) on a dry basis. From SASS train measurements.

[b] Silver and Thorium not detected in any test. Silicon not measured due to analytical problems.

[c] Not reported due to analytical problems or value below detection limit.

Another finding of note was that significant amounts of some elements entered the scrubber system with the lime. Elements such as Al, Be, Co, Ti, V, and Zn fall into this category. The elements As, Cu, Mn, and Hg entered the system in about equal amounts in the lime and in the flue gas. Although the errors associated with the trace elemental material balances used as a check of these measurements are fairly large, the results suggest that the alkaline additive may be a significant source of some of the trace elements eventually discharged from an $SO_2$ system.

**Organic Emissions** – A semiquantitative analysis survey technique was used for identification of organic compounds including polar organics, nonpolar organics (normal alkanes) and polynuclear aromatic hydrocarbons (PAH). Polar and nonpolar organics were determined by gas chromatography. If organic compounds were found in sufficient quantities (>1 ppm), a combined gas chromatographic/mass spectrometric analysis procedure was then used for PAH compound identification.

Gaseous hydrocarbons ($C_1$ to $C_6$ boiling point range) were emitted at levels of about 1 to 2 ppm. The scrubber had no apparent effect on these emissions. Most other organic material emission levels in both gas and liquid streams were lower than detectable levels for most of the tests. The detection limits are typically much lower than levels established by the EPA at which exposure for limited duration is judged not to cause adverse health or ecological effects. The organic compound recovery procedures developed for the program were determined to exhibit an efficiency of about 50 per cent for samples spiked to concentrations well above the concentrations found in the samples. These samples were spiked during field testing and subsequently analyzed in the laboratory. Significant sampling and analysis improvements need to be made before reliable organic emission information can be collected.

**Other Gaseous Emissions** – Other unregulated gaseous emissions measured included $H_2SO_4$, HCl, HF, and CO. The scrubber removed 39 to 78 per cent of the inlet $H_2SO_4$, 94 to 99 per cent of the HCl, and 93 to 99 per cent of the HF. Inlet concentration values were 4 to 19 ppm for $H_2SO_4$, which correspond to 0.2 to 0.7 per cent of the inlet $SO_2$ concentrations. Inlet concentrations were 26 to 57 ppm for HCl and 7 to 18 ppm for HF. Carbon monoxide was emitted at levels of less than 2 to about 8 ppm. The scrubber had no apparent effect on CO emissions.

## Scrubber Process Chemistry and Scrubber Performance

**Scrubber Chemistry Characteristics** – The Conesville Unit 5 scrubber operates with a high liquid phase alkalinity, primarily due to the high magnesium content of the lime additive. Liquid phase alkalinity is related to the $SO_2$ absorption capacity of a liquid and reflects the amount of alkaline material which is actually dissolved in the liquid. The recycle slurry always contained more than enough dissolved alkalinity to absorb the $SO_2$ present in the gas phase. Therefore, solids dissolution in the absorber is not a limiting factor. The high $SO_2$ removal observed (in excess of 90 per cent) is consistent with the scrubber process chemistry characteristics identified for this system.

Magnesium concentration levels in the recycle slurry stream were about 3,000 ppm which are typical for a magnesium-enhanced lime scrubber. Dissolved chloride levels in the recycle slurry and slurry drawoff streams were in the range of 1,000 to 1,800 ppm.

**$SO_2$ Removal** – Nearly all of the $SO_2$ removal occurred in the absorber section of the scrubber. Sulfur dioxide removal in the presaturator spray section was calculated to be 1 to 2 per cent of the total $SO_2$ removed. Sulfur dioxide removal in the mist eliminator was calculated to be less than 1 per cent.

A mass transfer area analysis of the scrubber absorber section showed that a significant amount of mass transfer area could be attributed to the droplets in the spray area and to the empty turbulent contact absorber (TCA) stage grids when compared to the area of the mobile packing spheres. Due to the high $SO_2$ absorption capacity of the recycle stream, it was concluded that the L/G could be reduced or the mobile packing spheres removed without significantly reducing $SO_2$ removal efficiency. Reduction in absorber recycle flow by 50 per cent did not significantly reduce the sulfur removal efficiency or alter the sulfite-to-sulfate oxidation ratio.

**Scaling Potential** — Relative saturations of $CaSO_4 \cdot 2H_2O$, $CaSO_3 \cdot 1/2\ H_2O$, $CaCO_3$, $Ca(OH)_2$, and $Mg(OH)_2$ were calculated for all scrubber process streams. The calculations indicated a low potential for scale formation in all streams except in the scrubber makeup and the mist eliminator wash streams. Calcium sulfate scaling was identified as a potential problem in the lime slurry preparation system and the mist eliminator. Calculations indicated that the scaling potential of the presaturator quench sprays was low. Based upon normal operating conditions, scaling in the absorber is not expected to be a problem. The calculated scaling potential values suggested that there is some potential for sulfite scaling in the mist eliminator. An approach was suggested for reducing the scaling potential in the mist eliminator by maximizing fresh water addition at that point. $CaCO_3$ and $Mg(OH)_2$ each have a high scaling potential in the lime slurry preparation system.

Liquid phase silicon material balances around the lime slurry preparation system suggest that silicon compounds (silica or silicates) are being precipitated. If precipitation occurs on equipment surfaces rather than on slurry particles, scaling could be a problem.

**Oxidation** — Overall oxidation of sulfite to sulfate in the scrubber averaged 22 ± 2 per cent of the $SO_2$ removed. More than 90 per cent of the oxidation occurred in the absorber section of the scrubber. No trend with gas phase oxygen content or other test conditions was observed. Scanning electron microscopy showed the typical rosette structure of lime scrubbing sludges containing predominantly calcium sulfite.

**Additive Reagent Ratio** — Conesville Module 5B is capable of operating at an additive reagent ratio, moles of lime and magnesium added per mole of $SO_2$ removed, in the range of 1.0 to 1.1 as demonstrated during the second test series. During the first test series, the reagent ratio was in the range of 1.2 to 1.3. Measured recycle stream pH values (about 7.2 in the first series in comparison to 6.3 in the second) reflected this difference.

The error associated with the lime reagent ratio determinations was estimated to be relatively high. The error estimates for these tests were ±15 to 20 per cent. While the error estimate may be slightly conservative, it is representative of the degree of accuracy obtainable for this measurement using stream flows and chemical analyses as the basis for the computation. Approximately 2.5 per cent of the lime additive is lost with grit removal.

**Scrubber Generated Particulate and Mist Eliminator Performance** — A combination of droplet photography and scanning electron microscopy along with several chemical analysis techniques were used in conjunction with information from several particulate and gaseous sampling techniques to characterize and quantify the amount of "scrubber generated particulate." A neglible amount of scrubber slurry entrainment was found, but a significant amount of sulfuric acid condensation occurred across the scrubber. Although the Conesville scrubber reduced total particulate emissions in nearly every test, this result is not necessarily applicable to new emission control systems which must meet the lower revised NSPS for particulate emissions of 0.03 $lb/10^6$ Btu.

Droplet photography results showed excellent mist eliminator performance in removing droplets 50 micrometers and larger. Virtually 100 per cent collection was realized for droplets in this size range in the first stage of the mist eliminator. The second stage in the Conesville scrubber essentially serves only as a polishing mist eliminator since the first stage is so effective. The droplet photographic technique appears promising as a tool for evaluating mist eliminator performance, but further development is required.

## Engineering Evaluation

**Operational Reliability and Availability** – The average availability of Conesville scrubber Module 5B from January 1977 through September 1979 was 40 per cent. During the period September 1979 through June 1980, Module 5B availability increased to 76 per cent. Overall Unit 5 scrubber system availability for 1981 was 82 per cent.

If major scrubber outages which resulted from labor problems, initial failure of major equipment components, and design changes are subtracted for the earlier period of low availability (40 per cent), a maximum estimated availability of about 70 per cent would be expected. This value compares favorably with that observed during more recent operation. The remaining 30 per cent of module unavailability was due to a variety of maintenance requirements, such as cleaning plugged lines, cleaning scrubber modules, and repairing equipment which had malfunctioned.

The average utilization factor for Module 5B from initial start-up through September 1976 was 26 per cent. During this same period, the boiler utilization was about 87 per cent. Low average availability, reliability, and operability are consistent with the documented low average utilization. The difference in utilization factors between the boiler and the scrubber reflects the amount of time that the scrubber could not be operated or was not operated. During the period September 1979 through June 1980, utilization of Module 5B increased to about 53 per cent.

**System Costs** – The final installed capital cost of the Conesville Unit 5 scrubber, exclusive of support facilities, was $23.81/kW in 1976 dollars. This represents approximately 30 per cent of the total scrubbing and waste disposal system cost of $62.78/kW. The total cost includes balance of plant costs for raw material receiving and storage, feed preparation, waste separation and disposal, increased induced draft fan capacity, general facilities, and erection of this equipment. The total estimated system cost based on actual costs and standard EPRI cost estimating assumptions for such items as Engineering Fees, Royalty Allowance, Preproduction Cost, Inventory and Initial Chemicals, Interest during Construction, and Land results in a total capital cost of $92.02/kW. Total yearly operating and maintenance costs ranged from 3.51 to 5.46 mills per kilowatt-hour during the initial three years of operation.

**Suggested System Improvements** – Several potential scrubber operational improvements were identified as part of the evaluation of the Conesville Unit 5 scrubber system.

- Operation of the scrubber with a pH control range similar to or possibly lower than the average 6.3 measured during the second test series. This will reduce lime consumption and still provide adequate $SO_2$ removal.
- Recovery of 2.5 per cent of the lime additive now lost as grit (lime which is not slaked) by installing a small ball mill to grind the material for injection into the recycle slurry tank.
- Removal of all or part of the TCA mobile sphere packing to permit increased gas flow through the scrubber or to reduce the system pressure drop. The cost savings estimated by the utility for Unit 5 resulting from this change is approximately $22,500 per year in fan operation cost and about $128,000 per year in maintenance and mobile sphere replacement costs. The TCA mobile sphere packing has been subsequently removed from all modules of Units 5 and 6. Preliminary efficiency tests performed by the operating utility on one of the scrubber modules during December of 1980 indicated a reduction in pressure drop with acceptable $SO_2$ removal efficiency. The utility has indicated that they have experienced reduced maintenance demands on the scrubbers by eliminating plugging problems encountered in the mobile sphere bed area.
- Reduction of the amount of slurry recirculated by operating with only two recirculation pumps to reduce pumping power requirements and scrubber pressure drop. This modification in the operation of the scrubber may not be feasible since the TCA mobile packing spheres have been removed.
- Modification of the mist eliminator wash system by adding a bleed line to the recirculation tank and by pretreatment of slaking dilution water to maintain suspended solids and silica at acceptably low levels. These modifications should help minimize nozzle pluggage and mist eliminator scaling.

- Modification of the slurry drawoff system to permit control based on slurry solids content. This should stabilize both scrubber chemistry and thickener operations. Recycle tank level would then be controlled by addition of mist eliminator blowdown as makeup water.

## COLSTRIP UNIT 2

### Test Conditions

All of the Colstrip Unit 2 scrubber testing was conducted at nearly full power operating conditions due to high load demands on the units. Flue gas flow through test Module 2A therefore varied only from about 350,000 to 400,000 acfm. Test conditions are shown in Table 5. The principal test variables included increasing the recycle slurry solids content up to a level of about 18 per cent from the routine operating level of about 10 to 12 per cent, and operating without addition of lime (Test 2) to supplement the alkaline fly ash collected in the venturi/spray tower scrubber. Only minor changes in liquid-to-gas (L/G) ratio (25 to 30 gallons/$10^3$ acf) were achieved during the testing. Scrubber vessel pressure drop remained in the range of 21 to 23 inches wg.

### Regulated Emissions Characterization

**Sulfur Dioxide ($SO_2$)** – Overall $SO_2$ removal efficiencies for scrubber Module 2A ranged from 83 to 88 per cent as shown in Table 6. Process chemistry measurements and calculations suggest that roughly comparable amounts of $SO_2$ were removed in the absorber and wash tray/mist eliminator sections. Module 2A $SO_2$ emission rate ranged from about 0.2 to 0.3 lb/MBtu during the test series.

**Particulate** – The Colstrip Unit 2 scrubbers exhibited an overall particulate removal efficiency ranging from 98.2 to 99.1 per cent as shown in Table 7. Particulate emissions were measured by EPA Method 5, the reference method for particulate. Based on single traverse Impactor and SASS Train Module 2A inlet and outlet measurements, particulate loading and removal for Module 2A appears representative of the overall system performance. Comparison of Module 2A inlet particulate mass loadings by Method 5 and the other particulate sampling techniques indicated good agreement among the alternate measurements. Overall particulate emissions from Unit 2 as measured by EPA Method 5 ranged from 0.030 to 0.045 lb/MBtu.

**Nitrogen Oxides ($NO_x$)** – The scrubber is ineffective for the removal of $NO_x$, and showed only a slight removal in some cases of about 5 to 10 per cent. An average scrubber module 2A emission rate of 0.50 lb/MBtu was measured during the test series.

### Unregulated Emissions Characterization

**Fine Particulate** – The inlet and outlet particulate size distributions for Colstrip scrubber module 2A are illustrated in Figure 6 along with the particulate pentration curve (ratio of outlet/inlet). All of the curves are typical of a wet particulate scrubber system and show no unusual trends. Penetration of 1 micrometer particulate was 0.1 per cent, but below 1 micrometer, the penetration increased sharply at about the same rate at which the particle size decreased (for example, for a 0.1 micrometer particle, penetration was about 10 times greater than for a 1 micrometer particle). However, some removal was achieved over nearly the entire particle size range.

Most of the particulate that penetrated the scrubber was fine particulate (less than 2 micrometers). The small size of the particulate is such that plume opacity can be high, even when mass emissions are low.

## TABLE 5. SUMMARY OF TEST CONDITIONS FOR COLSTRIP UNIT 2

| Test | System Conditions |  | Scrubber Module 2A |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Flue Gas at Scrubber Inlet |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | Boiler Load MW | (%) | Flow Rate $m^3/s$ | (kacfm) | Temperature C | (F) | $H_2O$(a) % | $O_2$(b) % | $CO_2$(b) % | Excess Air(c) % | Scrubber $\Delta P$(d) kPa | (in. wg.) | Liquid Rate m/s | (gpm) | L/G Ratio(e) $\frac{m^3}{km^3}$ | $\left(\frac{gal}{kacf}\right)$ | Recycle Slurry pH | Recycle Slurry Solids % | Molar(f) Reagent Ratio |
| 1 | 320 | (89) | 250 | (530) | 149 | (300) | 9.2 | 4.8 | 15.1 | 29.6 | 5.23 | (21.0) | 0.77 | (12,200) | 3.7 | (27) | 3.73 | 11.1 | 1.14 |
| 2 | 321 | (90) | 250 | (530) | 143 | (289) | 9.1 | 5.6 | 14.3 | 36.0 | 5.65 | (22.7) | 0.73 | (11,600) | 3.4 | (25) | 3.79 | 17.8 | 1.01 |
| 3 | 319 | (89) | 218 | (461) | 135 | (275) | 10.5 | 4.7 | 14.5 | 28.3 | 5.58 | (22.4) | 0.76 | (12,100) | 3.9 | (30) | 3.73 | 16.5 | 1.04 |

(a) Wet basis.

(b) Dry basis.

(c) Based on measured Module 2A inlet $O_2$.

(d) Total scrubber vessel pressure drop including venturi, mist eliminator, and wash tray sections.

(e) Liquid-to-gas (L/G) ratio calculated using measured liquid rate and saturated gas flow rate at scrubber conditions.

(f) Overall reagent ratio based on moles of calcium and magnesium added and sulfur removed (estimated error is ±0.3). Lime additive accounts for about 10 per cent of the total alkalinity in Tests 1 and 3, the balance of the alkaline material originates from the fly ash collected in the scrubber. No supplemental lime was added during Test 2.

## TABLE 6. FLUE GAS SULFUR DIOXIDE ($SO_2$) CONCENTRATIONS AND SCRUBBER REMOVAL EFFICIENCY FOR COLSTRIP SCRUBBER MODULE 2A[a]

| Test | Inlet |  |  | Outlet |  |  | $SO_2$ Removal[b] |
|---|---|---|---|---|---|---|---|
|  | ppm | ng/J | (lb/$10^6$ Btu) | ppm | ng/J | (lb/$10^6$ Btu) | (per cent) |
| 1 | 673 | 613 | (1.43) | 112 | 105 | (0.244) | 82.9 |
| 2 | 735 | 709 | (1.65) | 108 | 123 | (0.285) | 82.7 |
| 3 | 641 | 589 | (1.37) | 75 | 71 | (0.166) | 87.9 |

[a] Values in parts per million by volume from continuous monitor data on a dry basis and averaged over the test period for Module 2A only. Values on a weight per fuel value basis were calculated by using a factor representing a ratio of the volume of dry flue gas generated to the calorific value of the fuel burned (EPA "F" factor method). This factor wa then adjusted to the actual excess air present in the flue gas as determined by the oxygen content.

[b] Based on lb/$10^6$ Btu values.

### TABLE 7. OVERALL MEASURED PARTICULATE CONCENTRATIONS AND COLLECTION EFFICIENCY FOR COLSTRIP UNIT 2 SCRUBBERS[a]

| Test | Inlet |  |  |  | Outlet[b] |  |  |  | Collection Efficiency[c] (per cent) | Opacity (per cent) |
|---|---|---|---|---|---|---|---|---|---|---|
|  | $mg/Nm^3$ | (gr/dscf) | ng/J | ($lb/10^6$ Btu) | $mg/Nm^3$ | (gr/dscf) | ng/J | ($lb/10^6$ Btu) |  |  |
| 1 | 2,850 (2,890)[d] | 1.24 (1.26) | 983 ( 996) | 2.28 (2.31) | 42.1 | 0.018 | 15.1 | .035 | 98.5 (98.5)[e] | – |
| 2 | 2,990 (3,750) | 1.31 (1.64) | 1,060 (1,330) | 2.46 (3.08) | 50.8 | 0.022 | 19.4 | .045 | 98.2 (98.5) | 17.0 |
| 3 | 4,080 (2,610) | 1.78 (1.14) | 1,420 ( 910) | 3.29 (2.11) | 35.4 | 0.016 | 12.9 | .030 | 99.1 (98.6) | 9.9 |

[a] Concentrations are based on EPA Method 5, sampling over a two to three hour period. Values in milligrams per dry normal cubic meter and grains per dry standard cubic foot are given at 20 C (68 F) and 760 mm Hg (29.92 in Hg). Values on a weight per fuel value basis were calculated by using a factor representing a ratio of the volume of dry flue gas generated to the calorific value of the fuel burned (EPA "F" factor). This factor was then adjusted to the actual excess air present in the flue gas as determined by the oxygen content.

[b] From samples taken in the stack which represent the combined contribution of all three modules.

[c] Based on $lb/10^6$ Btu values.

[d] Values in parentheses are for Module 2A inlet by Method 5.

[e] Values in parentheses are the collection efficiency across Module 2A and the stack.

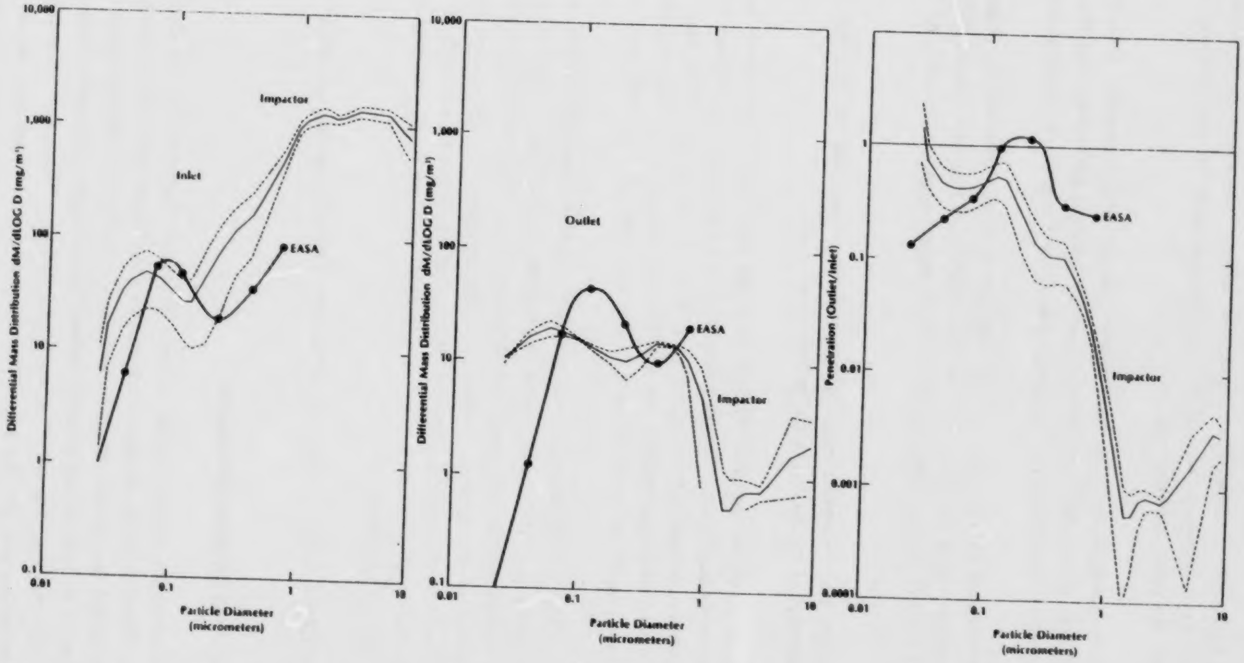


Figure 6. Colstrip Scrubber Module 2A Inlet and Outlet Particulate Size Distributors and Penetration (Outlet/Inlet) Measured with an Electrical Aerosol Size Analyzer (EASA) and a University of Washington Mark 20 Impactor. (Dashed Lines Indicate One Standard Deviation from the Average.)

**Trace Elements** – Trace elements entering and leaving the scrubber were measured by elemental analysis of samples collected from gaseous, liquid, slurry, and solids streams. Most of the elements usually considered present in non-volatile form were removed with an efficiency ranging from about 60 to more than 99 per cent as shown in Table 8. These elements included aluminum, barium, boron, cobalt, copper, iron, manganese, phosphorus, silicon, strontium, titanium, vanadium, and zirconium.

Penetration or low removal across the scrubber was observed for some of the elements normally considered "volatile" (chromium, nickel, and zinc). However, one of the two measurements for zinc indicated about 95 per cent removal by the scrubber while the other indicated high penetration.

Analytical difficulties were encountered with the trace elements which were frequently present in concentrations near their lower detection limits. Of the 54 trace element material balances performed, less than half of them met acceptance criteria. This illustrates the difficulty of establishing emission limits for this class of elements.

The data on elemental penetrations as a function of particle size generally followed the shape of the total mass penetration. The only exceptions were As, Se, and V which showed penetrations greater than one for sizes less than 0.1 micrometer, and Cu which showed penetration over the entire range. An example of the data is shown in Figure 7.

The predominant source of the trace elements entering the scrubber system was the inlet flue gas. Very little lime is added to this system since most of the alkalinity comes from the fly ash.

**Organic Emissions** – Organic materials emission levels in both gas and liquid streams were typically very near or below detectable levels for all measurements. The detection limits were typically much lower than levels established by the EPA at which exposure is judged not to cause adverse health or ecological effects. Based on the low concentrations for some of the organic materials detected, the scrubber had little effect on these emissions. Gaseous hydrocarbons ($C_1$ to $C_6$ boiling point range) were emitted at levels between about 0.1 and 0.5 ppm.

**Other Gaseous Emissions** – Other unregulated gaseous emissions measured included sulfuric acid ($H_2SO_4$), hydrochloric acid (HCl), hydrofluoric acid (HF), and carbon monoxide (CO). Sulfuric, hydrochloric, and hydrofluoric acid were present in very low concentrations, near their detection limits. The low values prevent conclusions from being drawn about the effect of the scrubber system on these emissions. There is some question that the low $H_2SO_4$ values may be an artifact of sampling since significant amounts of particulate sulfate were measured in the solid material collected by the $H_2SO_4$ sampling train. It is possible that the $H_2SO_4$ reacted with the calcium alkali in the ash either before or during sampling.

Carbon monoxide was emitted at levels of about 15 to 50 ppm. The scrubber had no apparent effect on CO emissions.

### Scrubber Process Chemistry and Scrubber Performance

**Scrubber Chemistry Characteristics** – The scrubber process chemistry characteristics for Colstrip are very different from those at Conesville. The differences are best illustrated by the concentrations of the principal dissolved species. First, the circulating slurry pH was measured to be less than 4 during the testing, which is very low. Dissolved chloride was relatively low in all tests for all process streams (below about 100 ppm). Dissolved magnesium, which is usually beneficial for $SO_2$ removal, was found at levels of 3,600 to 5,700 ppm in the recycle slurry bleed stream. The major source of magnesium was the fly ash. Dissolved potassium and sodium, which are also beneficial for $SO_2$ removal, were present at relatively low concentrations compared to magnesium. Sodium was present at a level of about 550 ppm in the recycle slurry and potassium was present in a comparatively minor amount of about 30 ppm.

## TABLE 8. FLUE GAS TRACE ELEMENT CONCENTRATIONS FOR COLSTRIP SCRUBBER MODULE 2A[a]

| Element[b] | Inlet, microgram/m³ |  | Outlet, microgram/m³ |  | Removal, per cent |  |
|---|---|---|---|---|---|---|
|  | Test 1 | Test 3 | Test 1 | Test 3 | Test 1 | Test 3 |
| Ag | <9 | <16 | <0.6 | 13.2 | – | – |
| Al | 540,000 | 614,000 | 2,200 | 2,600 | 99.6 | 99.6 |
| Au | <20 | <48 | <2 | 1.2 | – | – |
| B | 73 | 88 | 19 | 29 | 73.6 | 67.0 |
| Ba | 20,000 | 23,000 | 340 | 660 | 98.3 | 97.2 |
| Be | <3 | <5 | <0.20 | <0.4 | – | – |
| Cd | <30 | <37 | 0.98 | 2.2 | – | – |
| Ce | <430 | <530 | <20 | <34 | – | – |
| Co | <30 | 6.9 | <2 | <3 | – | >71.0 |
| Cr | 5.7 | 7.3 | 13 | 16 | –123 | –122 |
| Cu | 490 | 480 | 11 | 18 | 97.8 | 96.4 |
| Fe | 130,000 | 29,000 | 660 | 640 | 99.5 | 97.8 |
| Ga | <220 | <320 | <5 | 13 | – | – |
| Ge | <260 | <370 | <14 | 19 | – | – |
| La | <9 | <16 | <0.7 | <1.9 | – | – |
| Li | <43 | <53 | <2 | 6.2 | – | – |
| Mn | 5,500 | 5,900 | 37 | 38 | 99.3 | 99.4 |
| Mo | <260 | <370 | <14 | <24 | – | – |
| Ni | <130 | 26 | 12 | 28 | – | 6.2 |
| P | 6,400 | 7,900 | 1,800 | 1,800 | 72.7 | 77.5 |
| Pb | <170 | <260 | <3.2 | <14 | – | – |
| Sb | <1,300 | <2,100 | <70 | <120 | – | – |
| Si | 33,000 | 227,000 | 1,250 | 1,000 | 96.2 | 99.5 |
| Sn | <390 | <530 | <20 | <34 | – | – |
| Sr | 21,000 | 17,400 | 380 | 340 | 98.2 | 98.0 |
| Ti | 25,000 | 29,000 | 200 | 210 | 99.2 | 99.3 |
| V | 220 | 36 | 17 | 15 | 92.3 | 59.1 |
| Zn | 75 | 2.8 | 3.7 | 210 | 95.1 | –7,400 |
| Zr | 1,000 | 1,200 | 4.5 | 2.7 | 99.6 | 99.8 |

[a] All concentrations are normalized to 20 C (68 F) and 760 mm Hg (29.92 inches Hg) on a dry basis. From SASS train measurements. Lower detection limits for elements vary depending on sample dilution factor.

[b] Thorium not detected in any test.

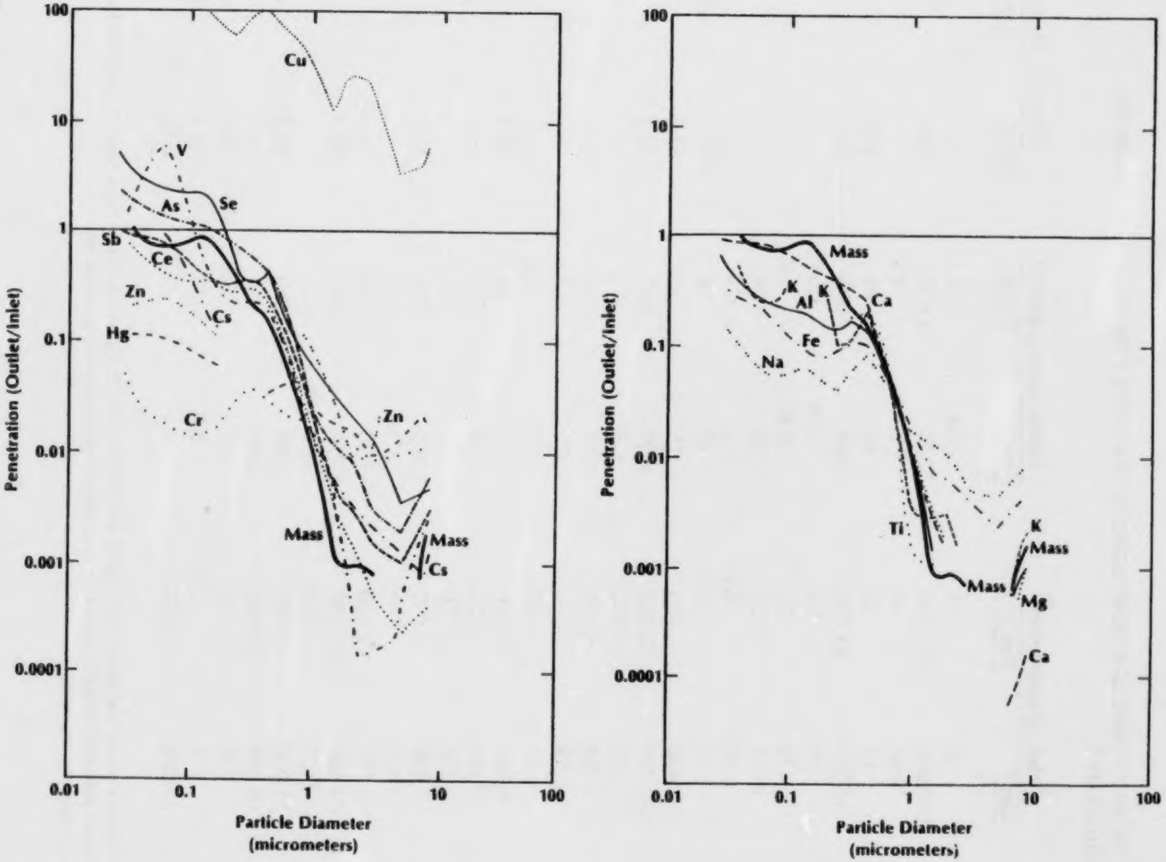


Figure 7. Colstrip Scrubber Module 2A Mass and Elemental Size Dependent Penetrations, Based On Elemental Analysis of Size-Segregated Impactor Samples.

Virtually all of the $SO_2$ removed is oxidized to sulfate. Dissolved manganese was found in the circulating slurry at concentrations of 50 to 70 ppm. Manganese is an efficient oxidation catalyst above a concentration of about 1 ppm. It appears as if the manganese may be responsible for the high oxidation rate. Thus, $SO_2$ removal is efficient, even at low pH, because with virtually no dissolved $SO_2$ there is very little vapor pressure of $SO_2$ over the solution. Under these conditions, there is a high driving force for mass transfer of $SO_2$ from the gas into the scrubbing liquor.

**$SO_2$ Removal** – An overall scrubber $SO_2$ removal efficiency of about 85 per cent was observed. Sulfur material balances around the system suggested that approximately 50 per cent $SO_2$ removal occurred in the venturi/spray section, and the remaining 35 per cent $SO_2$ removal occurred in the wash tray and mist eliminator sections. However, the errors associated with these calculations are high, related to inaccuracies in the measurement of flows into and out of the wash tray and the uncertainty in estimating the amount of slurry carryover into the wash tray section from the spray section. Calculation of equilibrium $SO_2$ vapor pressures indicate adequate driving force for $SO_2$ removal in the wash tray section. Since oxidation is a principal driving force for $SO_2$ removal in the Colstrip scrubber, it is judged reasonable that not all of the $SO_2$ removal occurs in the venturi/spray section since only limited acid-base reactions occur at the low pH conditions present in the scrubber. Conditions are then favorable for additional $SO_2$ removal by oxidation in the wash tray section where substantial liquid holdup occurs. These results indicate that scrubbers containing wash trays must be properly designed to minimize the potential for scaling, particularly for systems where significant $SO_2$ removal might occur in this region.

Because of the high oxidation, the driving force for $SO_2$ removal in the venturi and spray sections is very large. The calculated equilibrium $SO_2$ vapor pressures (ranging from 2 to 8 ppm) of the liquid in the venturi/spray section were significantly less than the estimated gas phase $SO_2$ concentrations of 260 to 440 ppm at the outlet of the venturi/spray section. The limited mass transfer area available in these sections probably limits the $SO_2$ removal in this area.

**Scaling Potential** – Scaling potentials for selected solids were evaluated for all of the process streams. Calcium carbonate relative saturation was relatively high in the upper mist eliminator spray, although the amount of material present is so low that significant scale build-up may not be a problem. In the event that a slow scale build-up in this area does occur, switching to an alternate source of water, such as fly ash pond return water, may remedy the problem.

For the three tests, gypsum saturation in the mist eliminator and wash tray section were near 1.1 which is below the critical saturation level of about 1.3 for scale formation. Gypsum saturation in the spray section was very near the critical scaling threshold level for one of the tests. Gypsum scaling could be a possibility in this system under abnormal operating conditions. Gypsum ($CaSO_4 \cdot 2H_2O$) is the only sulfur-containing solid precipitated in the Colstrip Unit 2 scrubber system.

Magnesium hydroxide relative saturation was high in the lime slurry stream, and this may cause scaling problems in the additive systems. No other potential scaling problems were identified.

**Oxidation** – The measured oxidation of sulfite to sulfate ranged from 98.5 to 99.7 per cent for the three tests. The high oxidation is important to the performance of this unit in maintaining a large "driving force" for $SO_2$ removal. Secondarily, the high oxidation produces a sludge that is easily dewatered, aiding in ash pond water recovery.

**Additive Reagent Ratio** – Colstrip Unit 2 is capable of operating at a very low reagent ratio (near 1.0), and nearly all of the alkalinity is provided by the alkaline constituents in the fly ash. Lime reagent ratio based on the lime slurry additive alone (not counting the alkalinity from the fly ash which accounts for the balance of the observed overall reagent ratio) is about 0.1 moles of calcium per mole of $SO_2$ removed. The estimated error associated with the reagent ratio determinations was found to be relatively high for these tests, about + 30 per cent. While the error estimate may be slightly conservative, it is representative of the type of accuracy obtainable for this measurement based on wet chemistry analyses and flow measurement techniques.

**Scrubber Generated Particulate and Mist Eliminator Performance** – Scrubber slurry entrainment at the inlet to the mist eliminator was calculated from a mass balance around the mist eliminator and wash tray system to be approximately 1 to 3 per cent of the recycle slurry flow. On the basis of particulate sulfate levels measured in the flue gas at the scrubber inlet and outlet and estimated droplet penetration through the mist eliminator, a significant portion (about one-third) of the particulate emitted from the scrubber could be entrained slurry.

Droplet photography results showed that the Colstrip scrubber mist eliminator exhibited only a fair removal efficiency for a chevron-type system. On the basis of the droplet photography measurements and supplemental laboratory measurements, only about 90 per cent removal efficiency would be predicted for a 50 micrometer droplet. Essentially 100 per cent mist eliminator penetration of droplets smaller than 30 micrometers in diameter is predicted.

### Engineering Evaluation

**Operational Reliability and Availability** – Each scrubber module at Colstrip is designed to treat 40 per cent of the design flue gas flow from one of the boilers, and no bypass is provided. If a scrubber module is taken off line, the boiler load must be dropped to below a maximum of 80 per cent of design load.

The Colstrip scrubbers have consistently exhibited availabilities over 90 per cent. Scheduled outages and annual overhauls have been the leading cause of scrubber outages. Availability is defined as the total hours that the scrubber system is available for operation divided by the total number of hours in a selected time period. The average availability of the Unit 2 scrubbers over the time period from January 1976 through January 1981 was approximately 86 per cent, which includes scheduled outages.

The reasons for scrubber outages were investigated. The months with scrubber availabilities under 50 per cent were months in which annual overhauls were performed. The availability of individual scrubber Module 2A, which was characterized in the test program, was also examined. Numerous miscellaneous minor problems with various scrubber equipment existed. However, as in the case of the overall unit availability, the major causes of scrubber outages were scheduled maintenance and inspection.

**System Costs** – The installed cost of the Colstrip Units 1 and 2 scrubbers was $69/kW in 1978 dollars. The scrubber operating and maintenance cost was reported by the utility to be 0.45 mills/kWh for 1977 and 1978. These costs account for about 15 per cent of the overall plant operating and maintenance cost, excluding fuel costs.

**Suggested System Improvements** – The Colstrip Unit 2 scrubber was found to be performing within requirements and without significant operational problems. Consequently, no major system improvements were identified. However, it seems unlikely that this type of wet venturi scrubber system could consistently meet the more restrictive current New Source Performance Standards for particulate with similar high availability and low level of operational problems.

It was concluded that the Colstrip scrubber system could operate just as efficiently and without scaling problems with limestone as the supplemental scrubber additive as with lime additive. However, since lime additive handling and preparation equipment is presently installed and lime comprises only about 10 per cent of the required alkalinity (the balance originating from the fly ash), such a change may not be cost effective for these existing units.

## CONCLUSIONS

Conclusions based on the characterization of the Conesville and Colstrip $SO_2$ removal systems should be viewed from two perspectives: emissions control and system performance evaluation.

### Emissions Control

Both scrubber modules evaluated appear capable of achieving, at least in the short term, $SO_2$ removals greater than those required by current NSPS regulations. Both the Conesville and Colstrip emission control systems also appear to be capable of significant particulate removal based on the inlet concentrations measured during these tests. It is uncertain, however, whether either system (the ESP and wet scrubber at Conesville and the venturi/spray absorber at Colstrip), as designed, would meet the current particulate NSPS. For the Conesville high sulfur coal, the presence of sulfuric acid can confound particulate emission measurements since, depending on the collection temperature, this material can be included as part of the mass emissions measured.

The Conesville scrubber appeared to have a significant impact on most trace elements, $H_2SO_4$, HCl, and HF emissions, and a negligible impact on $NO_x$, CO, and organic materials emissions. The presence of condensed sulfuric acid created significant problems with fine particulate sampling and measurement of trace elements as a function of particle size. Significant improvements in the techniques for these measurements and the measurement of organics are needed before reliable information on these subjects can be collected.

The Colstrip scrubber appeared to achieve at least some reduction of trace element emissions as a function of particle size and fine particulate (<2 micrometer diameter). Little impact was seen for $NO_x$, CO, and organics. The amounts of $H_2SO_4$, HCl, and HF at the module inlet were so low that the estimated system removal was not meaningful. Sampling problems were less at Colstrip but still suggested the need for improvements in sampling techniques.

### System Performance Evaluation

The Conesville scrubber system provided high $SO_2$ removal across the module, but the presence of a gas bypass essentially controls the overall $SO_2$ emissions when the module is operating properly. The high magnesium lime provides the capability of very high scrubber module $SO_2$ removals. The alkalinity contained in the slurry is so high that calculations indicated that the mobile contacting spheres in the absorber could be removed without significantly affecting $SO_2$ removal. The utility has since removed the spheres in Units 5 and 6 with no apparent degradation in $SO_2$ removal. Removal of the spheres has reduced maintenance on the scrubber modules which has contributed to improved availability. Another operational improvement would be a reduction of the liquid-to-gas (L/G) ratio of the recirculating slurry. Testing confirmed that a 50 per cent reduction in L/G had a minimal impact on $SO_2$ removal. These changes can result in significant energy and cost savings for any utility using or considering such a scrubber system.

A similar design impact was found at Colstrip, where calculations indicated that the mist eliminator system might be removing significant amounts of $SO_2$ due to the oxidation removal mechanism that promotes $SO_2$ removal. Examination of fly ash for the presence of oxidizing agents such as manganese and evaluation of the mass transfer capabilities and scrubber process chemistry could provide insight into future designs and a better utilization of the high available alkalinity in the fly ash from some coals.

Also identified for both scrubber systems were areas where scaling might occur and how it could be avoided. These techniques are applicable to any wet scrubber to reduce operating costs due to maintenance outages.

Scrubber-generated particulate (slurry entrainment) did not appear to be significant for either of the scrubbers; however, there was a significant difference in the measured mist eliminator system moisture removal efficiencies. This difference suggests that further research might be advisable to assure proper design and operation of such systems.

Both units appear to be fairly typical currently operating wet scrubber designs. Conesville had low system availability during the first few years of operation, but availability was substantially improved during 1981 and current values reported by the utility approach 90 per cent.

The techniques used at these two test sites appear capable of evaluating a scrubber system to aid in troubleshooting problem areas and optimizing system operations in ways that should apply to any FGD system. Future studies of this type are expected to be most profitably directed at units experiencing operational problems. Several problems were experienced while collecting data on a wide range of currently unregulated emissions. The problems were related to difficulties in achieving material balance closures and inconsistent results for trace element concentrations, fine particulates, and organics. These difficulties emphasize the need for development and demonstration of improved sampling and analysis methodologies for these species before emission restrictions are promulgated.

## ACKNOWLEDGMENTS

Permission to test the Conesville Unit 5 scrubber by Columbus and Southern Ohio Electric Company and the Colstrip Unit 2 scrubber by Montana Power Company is most gratefully acknowledged. The authors wish to express their appreciation to Jeffrey C. Lytle of Columbus and Southern Ohio Electric Company and Carlton D. Grimm of Montana Power Company for their cooperation in the scrubber test programs and data collection efforts.

The authors would also like to acknowledge the contributions of the following organizations which participated in the project and provided field sampling, laboratory analysis, and data evaluation in support of the testing and scrubber system evaluations.

TRW Inc.; Redondo Beach, California
PEDCo Environmental; Cincinnati, Ohio
Meteorology Research, Inc.; Altadena, California
Southern Science Applications, Inc.; Dunedin, Florida
Calfran Industries; Springfield, Massachusetts
Envirotech/Eimco; Salt Lake City, Utah

# Panel: Reliability and Maintenance

Thomas M. Morasky, Chairman
Reliability and Nonrecovery Systems
Electric Power Research Institute
Palo Alto, CA

# PANEL: RELIABILITY AND MAINTENANCE
# HOW RELIABLE SHOULD AN FGD SYSTEM BE?

by: David W. Joos
Black & Veatch Consulting Engineers
Kansas City, MO 68144

## ABSTRACT

The ultimate goal of an electric utility is to provide power to its customers at the lowest possible cost. Although high reliability and availability are generally analogous to low cost, this is not always the case, and it must be remembered that the ultimate goal is not high availability, but low cost. The cost of availability must be weighed against the cost of unavailability.

The costs of availability are:

- Higher capital cost--redundant equipment, larger capacity equipment, higher quality equipment, and higher engineering cost
- Higher maintenance cost--frequent preventive maintenance and larger staff

The costs of unavailability are:

- Higher operating cost--purchased power and inefficient operation
- Higher maintenance cost
- Fines and penalties
- Intangibles--public opinion and personnel morale

How can these effects be quantified to determine whether availability improvement modifications are justifiable during the design stage or as a retrofit?

Example 1: Should availability or design removal efficiency be improved to comply with $SO_2$ emission regulations based on a 30-day rolling average removal efficiency or emission rate?

- Discussion of paper submitted to the Seventh FGD Symposium (not yet accepted), "Evaluation of Alternative FGD System

Removal Efficiency and Reliability Improvement Options at APS Four Corners Units 1, 2, and 3."

Example 2: How many spare scrubber modules should be installed?

- Depends on module availability, module capacity, plant load model, replacement power cost, and scheduled maintenance requirements.
- Use binomial expansion with plant load model to evaluate.

----------

The work described in this abstract was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

# FAILURE MODE ANALYSIS FOR LIME/LIMESTONE FGD SYSTEMS

by: Harvey S. Rosenberg
Battelle Columbus Laboratories
Columbus, OH 43201

## ABSTRACT

Battelle's Columbus Laboratories has been conducting an extensive investigation of FGD systems since January 1974 as part of a group research program that was originally underwritten by EPRI. Additional support was later obtained from API and a number of individual companies in the U.S. and overseas. As part of this ongoing program, we have visited over 100 FGD installations for which formal assessment reports have been prepared.

In a current program for the U.S. Department of Energy, Battelle is identifying and analyzing the causes of failure in lime/limestone FGD systems in order to recommend appropriate remedial measures to system users. Information was collected on FGD system components at 37 utility plants. Each component has been analyzed in terms of the total number of failures reported during the past year, the impact of the failures on the FGD system, and the total downtime during the past year. The results indicate that the leading contributors to unreliability are ductwork, mist eliminators, stacks, $SO_2$ absorbers, pipes, and valves.

Ductwork, stack, and pipe and valve failures cause downtime for the entire FGD system, while mist eliminator and $SO_2$ absorber failures cause downtime for a given module in the FGD system. Therefore, much of the downtime for the latter two components can be eliminated by the use of spare modules. A spare module can be either a physical spare where an extra module(s) is designed into the system, or an operational spare where a module(s) is needed for full load but is repaired only during periods of reduced load.

The results also show that ductwork and stack linings have low incidences of failure per unit or plant but high downtimes per failure, while pipes and valves fail often but have low downtimes per failure. Stack lining and outlet duct lining failures have been identified as the major failure modes contributing to FGD system unreliability.

-----------

Although the research described in this abstract has been funded wholly or in part by the U.S. Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

## RELIABILITY OF LIME/LIMESTONE FGD TECHNOLOGY

by: Bernard A. Laseke
PEDCo Environmental, Inc.
Cincinnati, OH 45246

### ABSTRACT

PEDCo Environmental is currently conducting two separate ongoing studies for the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Energy (DOE) which focus on the collection of design, performance (reliability and $SO_2$ removal efficiencies) and cost data for FGD systems operating on coal-fired utility boilers. The Utility FGD Survey Program is an ongoing investigation which has been conducted for EPA for the past eight years. The Failure Mode Analysis for Lime/Limestone FGD systems is a two-year intensive investigation of the reliability of commercial lime/limestone FGD systems operating on coal-fired utility boilers. This study is being conducted with Battelle for DOE/Morgantown Energy Technology Center (METC).

These two studies provide the following types of detailed data for lime/limestone FGD systems in service on coal-fired utility boilers: Capital and annual costs; system/subsystem reliability; operation and maintenance; unit service; fuel consumption and composition; and $SO_2$ removal efficiency.

Of the lime/limestone FGD systems currently in commercial service on coal-fired utility boilers, sufficient data are available for a select population of systems to conduct the following analyses:

1. Determine trends in overall system availability for the period of 1978 to 1981.
2. Calculate cost effectiveness in terms of dollars per ton of $SO_2$ removed in order to determine how well systems are operating and why.

## FLUE GAS DESULFURIZATION RELIABILITY IMPROVEMENT AT THE BRUCE MANSFIELD PLANT

by: Russell C. Forsythe
Pennsylvania Power Company
New Castle, PA 16103

### ABSTRACT

The Pennsylvania Power Company-operated Bruce Mansfield Plant is a coal-fired power plant consisting of two (2) 780 MW and one (1) 800 MW net dependable generation capacity units. All three units are equipped with wet lime flue gas desulfurization systems with no by-pass. Unit No. 1 began full commercial operation on June 1, 1976, Unit No. 2 on October 1, 1977, and Unit No. 3 on September 29, 1980.

Since beginning full commercial operation, the units have had equivalent availabilities of 63.98%, 67.37%, and 78.44% through December 1981. The flue gas desulfurization systems have had equivalent availabilities of 90.04%, 90.8%, and 96.4% through December 1981. The FGD availabilities are a direct measurement of the reliability of the systems.

The FGD system experienced several problems during the start up and the first few years of operation which limited the FGD reliability. Problems such as stack liner failures, I.D. fan housing failures, and various control problems had a direct effect on FGD reliability. By constantly working with the system, determining the root cause of the problems and evaluating possible corrective actions, we have been able to improve the FGD reliability.

-----------

The work described in this abstract was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

---

## POSITIVE THOUGHTS ABOUT FGD RELIABILITY

by: James H. Buckner
Tennessee Valley Authority
Chattanooga, TN 37401

### ABSTRACT

The relatively short history of flue gas cleaning system has had somewhat of a negative ring. Most of the information provided by utilities

has dwelled on system or equipment failures rather than successes. Early installations typically experienced poor performance, low availabilities, and high O&M costs. Flue gas cleaning systems being currently installed should perform reliably if properly designed, operated, and maintained. Controls, hardware, and materials of construction have now been developed specifically for this purpose.

Let us take a positive look at areas that can help produce a successful flue gas cleaning operation. Absorber design, mist eliminator chemistry, coatings, materials of construction, piping designs, configuration of equipment, and location of draft fans are factors which can and do affect reliability and operability. Proper training of operators and maintenance personnel is essential. Probably the most significant single factor contributing to a successful operation and continuous compliance is simply an honest commitment to make the system work. Once this commitment is made, solutions to almost any problem can be satisfactorily resolved.

-----------

The work described in this abstract was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

## DESIGN FEATURES OF A HIGHLY RELIABLE FGD SYSTEM

by: Christopher P. Wedig
Stone & Webster Engineering Corp.
Boston, MA 02107

### ABSTRACT

A highly reliable FGD system is the result of superior operation, maintenance, and design. Many design features contribute to a highly reliable FGD system.

Some of the mechanical design features that must be considered are as follows: (1) Sparing of scrubber modules, pumps of every service, reagent prep equipment, and dewatering equipment; (2) alloy scrubber modules and outlet duct work when applicable; (3) limit flue gas linear velocity; (4) use alloy or rubber-lined slurry pipe and rubber-lined slurry pumps; (5) limit slurry velocity in pipes; and (6) limit slurry pump impeller tip speed to 5,100 ft./min. and booster fan tip speed to 22,000 ft./min.

Careful consideration must also be given to the instrumentation and controls of a highly reliable scrubbing system. In this regard the following design features should be considered: (1) Spare pH probes with ultrasonic cleaning; (2) spare sulfur dioxide monitor; (3) spare flue gas pressure and gas flow indicators; (4) use of solid state electronics; and (5) minimize use of slurry control valves.

In addition, important design features of the electrical side of the FGD system should be considered as well as structural considerations.

## Session 5: FLUE GAS TREATMENT (COMBINED $SO_x/NO_x$) REMOVAL

J. David Mobley, Chairman
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

# $SO_x$ AND $NO_x$ REMOVAL FOR COAL-FIRED BOILERS IN JAPAN

Jumpei Ando

Faculty of Science and Engineering
Chuo University, Tokyo

## ABSTRACT

Combined $SO_x$ and $NO_x$ removal from flue gas from coal combustion has become more and more important with the increase of coal-fired boilers. Stringent regulations in Japan necessitate the combined removal even for flue gas containing about 200 ppm each of $SO_x$ and $NO_x$ derived from controlled combustion of low-sulfur coal. Flue gas cleaning, including selective catalytic reduction (SCR) of $NO_x$, electrostatic precipitation, and the wet limestone-gypsum flue gas desulfurization (FGD) process, has been applied successfully to three coal-fired boilers, removing 50-85% of $NO_x$, 99.9-99.95% of particulates, and 90-95% of $SO_2$. Thirteen similar cleaning plants are under construction for coal-fired boilers.

Ammonia at the SCR reactor outlet is maintained below 5 ppm so as to give no adverse effect on FGD and the quality of fly ash, although wastewater treatment to remove ammonia may be required in certain regions. Cost of SCR is about one-third that of FGD by the limestone-gypsum process in both investment and operation. The power generation cost, including the flue gas cleaning and wastewater treatment, is less than that with low-sulfur oil without flue gas cleaning. The development of the combined cleaning system for coal has contributed significantly to save oil and to solve the energy problem in Japan. Simultaneous $SO_x$ and $NO_x$ removal by the electron beam and activated carbon processes has been tested.

## 1. INTRODUCTION

Ambient $SO_2$ concentrations in Japan have been lowered remarkably to meet the stringent air quality standard of 0.04 ppm daily average (equivalent to 0.02 ppm yearly average) in nearly all regions due to the strenuous efforts of $SO_x$ abatement including the construction of more than 1400 commercial FGD units.

For $NO_x$ abatement, combustion modification has been applied to more than 100,000 gas sources which provide about 95% of total flue gas. $NO_x$ concentrations in flue gases from utility boilers have been reduced by combustion modification to 200-300 ppm for coal, 80-120 ppm for oil, and 40-80 ppm for gas. Automobile emissions have been controlled by the most stringent regulations, including 0.25 g $NO_x$/km for gasoline-engined passenger cars. The fact that ambient $NO_2$ concentrations exceed the strict standard (Table 1) in several regions indicates that flue gas treatment (FGT) for $NO_x$ removal is needed.

TABLE 1. AMBIENT AIR QUALITY STANDARDS, ppm

| | $SO_2$ | | $NO_2$ | |
|---|---|---|---|---|
| Country | Daily average | Yearly average | Daily average | Yearly average |
| Japan | 0.04 | 0.02 | 0.04-0.06 | 0.02-0.03 |
| U.S.A. | | 0.03 | | 0.05 |
| West Germany | | 0.05 | | 0.05 |

A recent Environment Agency (Japan) report(1) claims that, to use coal, the combustion gas should be cleaned to a level equal to that of the gas from low-sulfur oil.

Many simultaneous $SO_x$ and $NO_x$ removal processes have been studied for several years. Some of the processes have been applied commercially to relatively small oil-fired industrial boilers (10-40 MW equivalent); they have not yet been applied to larger gas sources because of problems with the processes. On the other hand, selective catalytic reduction (SCR) of $NO_x$, using ammonia and a catalyst at 300-400°C to convert $NO_x$ to $N_2$ and $H_2O$, has been developed and applied to more than 130 gas sources, including coal-fired utility boilers. Table 2 shows major coal-fired utility boilers in operation and the $SO_x$ and $NO_x$ concentrations in their flue gases.

This paper mainly describes FGD and combined SCR/FGD for coal-fired boilers; it briefly describes simultaneous $SO_x$ and $NO_x$ removal processes.

TABLE 2. EXAMPLES OF $NO_x$ AND $SO_x$ EMISSIONS FROM COAL-FIRED UTILITY BOILERS

| | | | | $NO_x$, ppm | | $SO_x$, ppm | | |
|---|---|---|---|---|---|---|---|---|
| Power company | Station | New (N) or retrofit (R) | Capacity, MW | Boiler out | SCR out | FGD in | FGD out | Reheater out |
| EPDC[a] | Isogo[b] | R | 265 | 200[c] | -- | 450 | 20 | 30 |
| EPDC | Takasago | R | 250 | 350 | — | 1500 | 100 | 140 |
| EPDC | Takasago | R | 250 | 350 | — | 1500 | 100 | 140 |
| EPDC | Takehara | R | 250 | 400 | 80 | 1700 | 100 | 140 |
| EPDC | Matsushima[b] | N | 500 | 300[d] | -- | 1000 | 60 | 100 |
| Chugoku Electric | Shimonoseki | R | 175 | 400 | 190[e] | 750 | 45 | 80 |
| Hokkaido Electric | Tomato-Atsuma[f] | N | 350 | 200[g] | 30 | 230 | 10 | 20 |

[a] Electric Power Development Company.

[b] Subjecting 75% of the gas to FGD.

[c] With DF-CN burner, two-stage combustion (TSC), and domestic low nitrogen coal (1% or less).

[d] Using imported coal with SGR burner, TSC, and flue gas recirculation (FGR).

[e] Can be lowered to 80 ppm when needed.

[f] Subjecting 25% of the gas to SCR and 50% of the gas to FGD.

[g] Using domestic coal with dual-register burner, TSC, and FGR.

# 2. FGD UNITS FOR COAL-FIRED BOILERS

## 2.1 Types of Lime/Limestone FGD Processes

All FGD units for coal-fired boilers in Japan use lime/limestone scrubbing, which may be classified in four types as shown in Figure 1 and Table 3. Type I is the throwaway sludge process, typical in the U.S.A. There is only one Type I unit: it is at Omuta and was constructed by Mitsui Miike Machinery Co. Other units use limestone and oxidize calcium sulfite to gypsum. To completely oxidize calcium sulfite to gypsum, it is usually necessary to lower the pH of the sulfite slurry to about 4. With a catalyst, complete oxidation is attained at a pH of about 5. Type II units lower the pH to about 5 using three scrubbers and a catalyst for oxidation. There are three Type II units: one owned by Mitsui Aluminum (Omuta unit No. 2) and two by EPDC at Takasago.

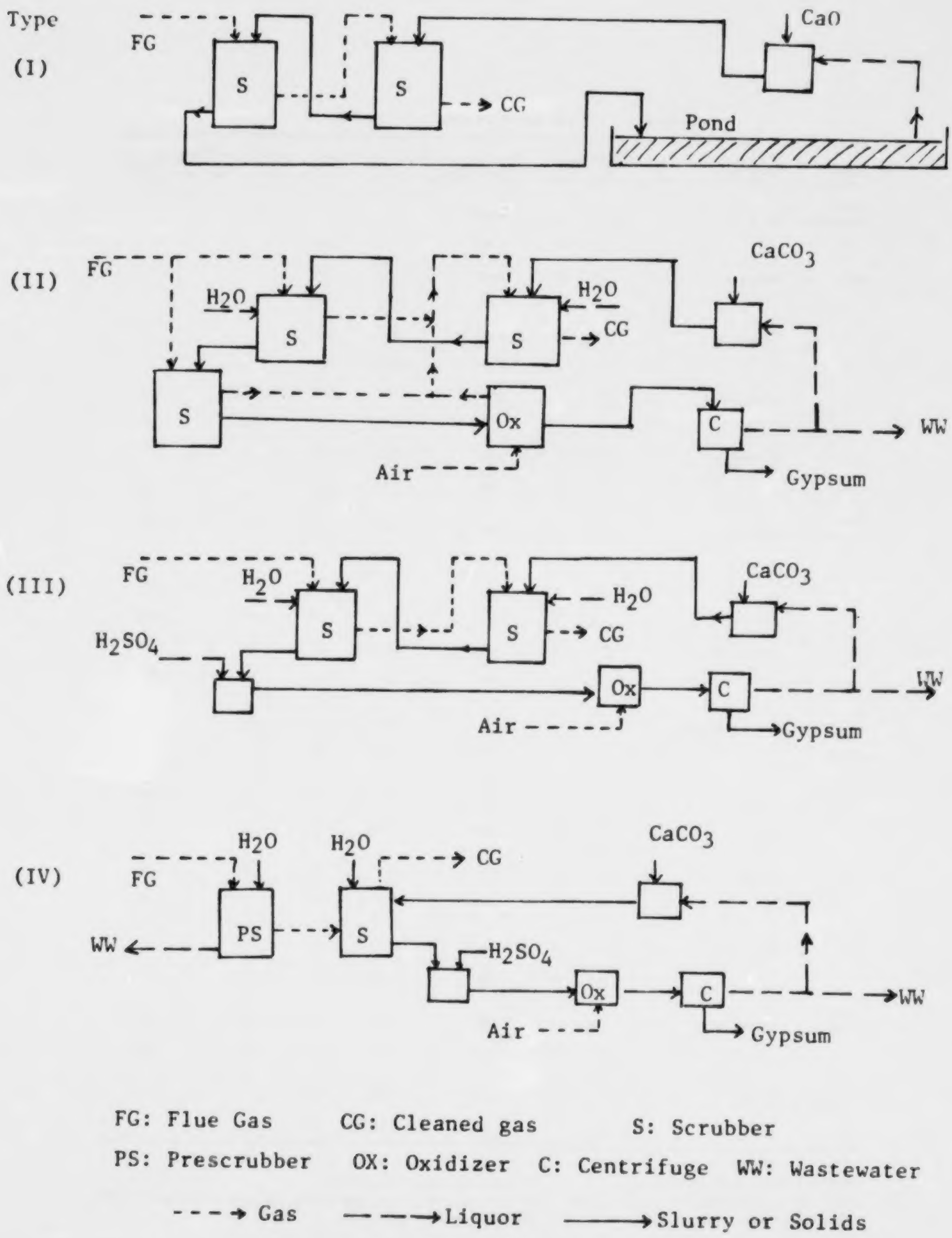


**Figure 1** Types of Commercial Wet Lime/limestone FGD Process for Coal-fired Boilers in Japan

TABLE 3. FGD AND SCR UNITS FOR COAL-FIRED BOILERS

| Owner | Plant Site | Boiler | | | FGD | | | SCR | |
|---|---|---|---|---|---|---|---|---|---|
| | | No. | MW | N/R[a] | Constructor | Completion | Type | Constructor | Completion |
| Mitsui Aluminum | Omuta | 1 | 156 | R | MMMC[b] | 1972 | I | | |
| - | - | 2 | 175 | N | MMMC | 1975 | II | | |
| EPDC | Takasago | 1 | 250 | R | MMMC | 1975 | II | | |
| - | - | 2 | 250 | R | MMMC | 1976 | II | | |
| - | Isogo | 1 | 265 | R | IHI[c] | 1976 | III | | |
| - | - | 2 | 265 | R | IHI | 1976 | III | | |
| - | Takehara | 1 | 250 | R | BHK[d] | 1977 | III | BHK, KHI | 1980 |
| - | - | 3 | 700 | N | IHI | 1983 | IV | BHK | 1983 |
| - | Matsushima | 1 | 500[e] | N | IHI | 1981 | IV | | |
| - | - | 2 | 500[e] | N | BHK | 1981 | IV | | |
| Chugoku Electric | Shimonoseki | 1 | 175 | R | MHI[f] | 1979 | IV | MHI | 1980 |
| - | Shin-Ube | 1 | 75 | R | MHI | 1982 | IV | MHI | 1982 |
| - | - | 2 | 75 | R | MHI | 1982 | IV | MHI | 1982 |
| - | - | 3 | 156 | R | MHI | 1982 | IV | MHI | 1982 |
| - | Mizushima | 1 | 125 | R | BHK | 1983 | IV | BHK | 1983 |
| - | - | 2 | 156 | R | BHK | 1983 | IV | BHK | 1983 |
| Hokkaido Electric | Tomato-Atsuma | 1 | 350[g] | N | BHK | 1980 | IV | BHK | 1980 |
| - | - | 2 | 600 | N | MHI | 1984 | IV | | |
| Kyushu Electric | Omura | 2 | 156 | R | MHI | 1982 | IV | MHI | 1982 |
| - | Minato | 1 | 156 | R | MMMC | 1983 | III' | MHI | 1983 |
| Joban Joint | Nakoso | 8 | 600 | N | MHI | 1983 | IV | MHI | 1983 |
| - | - | 9 | 600 | N | MHI | 1983 | IV | IHI | 1983 |
| Tohoku Electric | Sendai | 2 | 175 | R | BHK | 1983 | IV | BHK | 1983 |
| - | - | 3 | 175 | R | BHK | 1983 | IV | BHK | |
| Tokyo Electric | Yokosuka | 1 | 265 | R | MHI | 1984 | IV | MHI | 1984 |
| - | - | 2 | 265 | R | MHI | 1984 | IV | MHI | 1984 |
| Shikoku Electric | Saijo | 1 | 175 | R | KHI[h] | 1983 | IV' | | |
| - | - | 2 | 250 | R | KHI | 1984 | IV' | | |

[a] New or retrofit.

[b] Mitsui Miike Machinery Company.

[c] Ishikawajima-Harima Heavy Industries.

[d] Babcock-Hitachi K.K.

[e] Subjecting 75% of the gas to FGD.

[f] Mitsubishi Heavy Industries

[g] Subjecting 50% of the gas to FGD and 25% of the gas to SCR.

[h] Kawasaki Heavy Industries.

Type III units have two-stage scrubbers and lower the pH of slurry at about 5 to about 4 by adding a small amount of sulfuric acid. Type III units require less investment cost than Type II units and may be preferred where sulfuric acid is available at a reasonable cost. There are three Type III units, all owned by EPDC: two at Isogo were constructed by Ishikawajima-Harima Heavy Industries (IHI) and one at Takehara was constructed by Babcock-Hitachi (BHK).

Type IV units have a prescrubber with a separate liquor loop and use sulfuric acid for pH control. The prescrubber: (1) removes fly ash in the gas to reduce erosion of the scrubber system and to increase the purity of the gypsum; (2) removes chloride and fluoride from the gas to protect the scrubber system from corrosion (the fluoride removal may also increase both $SO_2$ removal efficiency and limestone utilization, possibly because fluoride reacts with limestone to form a coat of insoluble calcium fluoride on the surface of the calcium carbonate particles); and (3) cools the gas to eliminate scaling in the scrubber.

Type IV units, developed by Mitsubishi Heavy Industries (MHI) since the 1960s, have been applied to more than 30 FGD units by MHI, mainly for oil-fired boilers; it was applied to a coal-fired boiler of Chugoku Electric at Shimonoseki in 1979. All of the limestone scrubbing units constructed since 1979 are Type IV, including those to be constructed by IHI and BHK (Table 3). The Type IV unit prescrubber treats a hot flue gas with an acidic liquor with a pH of about 1, containing considerable amounts of chloride, fluoride, and fly ash. Therefore, the prescrubber requires highly corrosion- and erosion-resistant materials; for example, silicon carbide is often used for the spray nozzles. However, the prescrubber substantially reduces troubles in the scrubber system. All units with a prescrubber--the units at Shimonoseki, Tomato-Atsuma, and Matsushima--have been operated with 100% reliability since their start-up (Table 4). The two scrubber systems for two 500 MW boilers at Matsushima are operated by only two persons per shift (one person each).

TABLE 4. OPERATING HOURS OF BOILER AND FGD (OCTOBER 1980 - SEPTEMBER 1981)

| | New (N) or retro-fit (R) | Hours | | | FGD performance, % | |
|---|---|---|---|---|---|---|
| | | Boiler Operation (A) | FGD Operation (B) | FGD called to operate (C) | Oper-ability (B/A) | Reli-ability (B/C) |
| Shimonoseki | R | 7918[a] | 7825 | 7825 | 98.8 | 100.0 |
| Tomato-Atsuma | N | 8275[b] | 8263 | 8263 | 99.9 | 100.0 |
| Matsushima (Boiler No. 1) | N | 3968[c] | 3968 | 3968 | 100.0 | 100.0 |

[a] Boiler underwent annual maintenance in March and April 1981.

[b] Boiler started operation in October 1980.

[c] January to June 1981. Boiler started operation in January 1981.

The two units to be constructed by Kawasaki Heavy Industries (KHI) for Shikoku Electric (Table 3) will use the magnesium gypsum process(3) with a prescrubber with a separate liquor loop (Type IV'). Chiyoda may construct two FGD units for coal-fired utility boilers by the jet bubbling limestone-gypsum process(3) using also a prescrubber with a separate liquor loop.

The only unit under construction by the limestone-gypsum process without a prescrubber is that by MMMC for the Minato Station of Kyushu Electric (Table 3). A single spray tower will be used for 90% $SO_2$ removal using a catalyst and also sulfuric acid for pH control (Type III').

Most of the U.S. systems have no prescrubber but have a stand-by scrubber which is not installed in Japan. Moreover, the $SO_2$ removal efficiency by limestone scrubbing seems lower than that with the Type IV system in Japan by which about 95% removal is attained without any additive such as adipic acid used in the U.S.A.

The prescrubber may not be preferred for throwaway sludge systems that can be operated without scaling in the unsaturated mode. For the gypsum by-producing process, the prescrubber may be preferred, because the overall cost of power generation (including FGD) may be lowered by the high reliability of the FGD system.

## 2.2 Scrubber Types and Operating Parameters

Table 5 shows the capacities, types of scrubbers, and operating parameters of FGD units for utility boilers. The two EPDC units at Matsushima currently treat nearly 80% of the flue gas from the 500 MW boilers, while Hokkaido Electric's unit at Tomato-Atsuma treats 50% of the flue gas from a 350 MW boiler. Other units treat 100% of the flue gas from the boilers they serve.

EPDC's five FGD units at Isogo No. 1 and No. 2, Takasago No. 1 and No. 2, and Takehara were constructed between 1975 and 1977 and use venturi scrubbers or combined venturi and perforated plate scrubbers which give a high dust removal efficiency but a large pressure drop (325-615 mm $H_2O$ across two scrubbers), resulting in a high power consumption (2.2-2.6% of the power generated by the boiler). The relatively low consumption at Isogo (2.2%) is due to the low inlet $SO_2$ concentration of 450 ppm.

Chugoku Electric's FGD unit at Shimonoseki, constructed in 1979 by MHI using a combined spray tower (semi-venturi) prescrubber and plastic-grid packed tower, gives a lower pressure drop and consumes less power (2.1%).

TABLE 5. OPERATING PARAMETERS OF FGD UNITS FOR COAL-FIRED UTILITY BOILERS (LIMESTONE-GYPSUM PROCESS)

| Owner<br>Station | EPDC<br>Isogo | EPDC<br>Takasago | EPDC<br>Takehara | EPDC<br>Matsushima | | Chugoku<br>Shimonoseki | Hokkaido<br>Tomato-Atsuma |
|---|---|---|---|---|---|---|---|
| Boiler No. | 1 | 1 | 1 | 1 | 2 | 1 | 1 |
| Capacity, MW | 256 | 250 | 250 | 500x3/4 | 500x3/4 | 175 | 350x1/2 |
| Gas treated, 1,000 $Nm^3/hr$ | 821 | 792 | 793 | 1,300 | 1,300 | 610 | 610 |
| FGD constructor | IHI[a] | MM[b] | BHK[c] | IHI | BHK | MHI[d] | BHK |
| FGD start-up | 1976 | 1975 | 1977 | 1981 | 1981 | 1979 | 1980 |
| Inlet $SO_2$, ppm | 450 | 1,500 | 1,730 | 1,000 | 1,000 | 730 | 230 |
| Inlet dust, $mg/Nm^3$ | 1,500 | 100 | 100 | 300 | 300 | 830 | 25 |
| 1st scrubber (prescrubber) | Venturi | Venturi | Venturi | Spray | Spray | Spray | Venturi |
| L/G, liter/$Nm^3$ | 7 | 6 | 2.5 | 3 | 3 | 3 | 2.2 |
| 2nd scrubber (scrubber) | Venturi | Venturi | PP[e] | Spray | Spray | Packed | PP[e] |
| L/G, liter/$Nm^3$ | 7 | 6 | 7 | 15 | 15 | 14 | 5 |
| Outlet $SO_2$, ppm | 20 | 100 | 100 | 60 | 60 | 45 | 10 |
| Outlet dust, $mg/Nm^3$ | 50 | 30 | 50 | 30 | 30 | 50 | 5 |
| $SO_x$ removal efficiency, % | 95.5[f] | 93.3[f] | 94.2[f] | 94.0[g] | 94.0[g] | 93.8[g] | 95.7[g] |
| Dust removal efficiency, % | 96.6 | 70.0 | 87.5 | 90.0 | 90.0 | 94.0 | 80.0 |
| Pressure drop, mm $H_2O$ | 360[h] | 325[h] | 615[h] | 145[i] | 133[i] | 240[h] | 450[j] |
| Wastewater, t/hr | 10 | 7.5 | 12 | 15 | | 15 | 2.2 |
| Power requirement, %[k] | 2.2 | 2.6 | 2.6 | 2.2 | | 2.1 | 1.7 |
| Gas reheating facility | OF[l] | OF[l] | OF[l] | GGH[m] | GGH[m] | GGH[m] | GGH[m] |

[a] Ishikawajima-Harima Heavy Industries.

[b] Mitsui Miike Machinery Company.

[c] Babcock-Hitachi K.K.

[d] Mitsubishi Heavy Industries.

[e] Perforated plate.

[f] 1-3% lower after reheating by oil-firing.

[g] About 90% after gas reheating by gas-gas heater.

[h] By scrubbers and mist eliminators.

[i] By scrubbers.

[j] By scrubbers, mist eliminators, and gas-gas heater.

[k] Percent of power generated.

[l] Oil firing.

[m] Gas-gas heater.

Hokkaido Electric's Tomato-Atsuma unit, constructed by Babcock Hitachi (BHK) in 1980, uses an improved scrubber with lower pressure drop and smaller power consumption than the Takehara unit constructed by BHK in 1977 (power consumption is 1.7% vs. 2.6%). The low power consumption is due to the improved design and the low inlet $SO_2$ concentration of around 230 ppm.

The two EPDC units at Matsushima, completed in 1981 by IHI and BHK for 500 MW boilers, use spray towers with a low pressure drop of 133-145 mm $H_2O$. The new EPDC unit for the Takehara No. 3 boiler, being constructed by IHI, also uses a spray tower. The power consumption of Matsushima No. 2 is 2.2%.

MHI used a spray tower absorber for the first lime-gypsum process unit (20 MW equivalent) constructed in 1964 but has used a plastic-grid packed tower since 1972 as the scaling problem was solved, because the packed tower can be more efficient than the spray tower. The spray tower may have a high efficiency for a large scrubber with a height of over 30 m, such as constructed recently at Matsushima and Takehara (No. 3). The operation of those large units and three 600 MW units to be constructed by MHI for Joban Joint Power and Hokkaido Electric (Table 3) with plastic-grid packed tower will show a good comparison of the scrubbers.

All of those units use finely ground limestone so that over 95% passes a 325 mesh screen at a stoichiometry of 1.00-1.05 to remove 94-97% of $SO_2$. Gas reheating adds a small amount of $SO_2$ so that the overall $SO_2$ removal efficiency is 90-95%. The reheating has been by oil-firing at Isogo, Takasago, and Takehara (No. 1) and by gas-gas heater (Ljungstrom heat exchanger) at the new units.

The dust removal efficiency of the scrubber systems ranges from 70 to 96%. EPDC's FGD units at Isogo are designed for over 95% dust removal efficiency because the boilers use low-sulfur coal for which the conventional cold-side electrostatic precipitator (ESP) is not highly efficient. On the other hand, the EPDC boilers at Matsushima and that of Hokkaido Electric at Tomato-Atsuma use hot-side ESPs which are efficient for low-sulfur coal; therefore, the 80-90% dust removal efficiency of the FGD unit is sufficient.

## 3. SELECTIVE CATALYTIC REDUCTION AND ITS COMBINATION WITH FGD

### 3.1 Selective Catalytic Reduction (SCR)

Ammonia selectively reacts with $NO_x$ in gases at 150-450°C in the presence of a catalyst and oxygen. SCR can be conveniently applied to boiler economizer outlet gas at 300-400°C.

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O$$

Early in its development, SCR had serious problems. The major ones were: (1) catalyst poisoning by $SO_x$ in the gas; (2) plugging of the catalyst by dust; (3) deposit of ammonium bisulfate on the catalyst at a low temperature (around 300°C or below) due to reduced boiler load; (4) ammonium bisulfate deposit in an air preheater downstream of the SCR reactor; (5) promotion of oxidation of $SO_2$ to $SO_3$ by the catalyst; and (6) erosion of the catalyst by fly ash from the coal.

Solutions of those problems include: Problem (1)--using base metal catlysts based on $TiO_2$ instead of $Al_2O_3$ or $Fe_2O_3$; Problem (2)--using parallel-flow catalysts or reactors such as honeycomb, plate, and tube catalysts or parallel passage reactors (soot-blow may be applied if needed); Problem (3)--maintaining the gas temperature above about 300°C by using economizer by-pass when needed; Problem (4)--keeping $NH_3$ leakage (ammonia in the SCR reactor outlet) at a low (e.g., below 5 ppm) level; Problem (5)--developing low-oxidation catalysts (depressing oxidation also helps solve Problems (3) and (4)); and Problem (6)--using moderate gas velocity, hard catalyst, and a device (e.g., a dummy spacer) for erosion prevention.

SCR is simple, and an SCR unit is usually operated automatically (without an operator).

Figure 2 shows the relationship of inlet $NH_3/NO_x$ mole ratio to $NO_x$ removal efficiency and $NH_3$ leakage. Usually $NH_3$ leakage is kept below 5 ppm to eliminate an ammonium bisulfate problem. For 80% $NO_x$ removal for flue gas from coal, a ratio of 0.85 and space velocity of nearly 3,000 $hr^{-1}$ may be used; for 90% removal, a ratio of 0.95 and space velocity of about 2,000 $hr^{-1}$ may be used. Flue gas from oil combustion can be treated with 30-50% less catalyst because a much more active catalyst (porous and soft) can be used.

Figure 3 shows the effect of boiler load on SCR performance. At a reduced load, gas temperature is lowered but $NO_x$ removal efficiency is raised because of the longer reaction time due to the reduced gas flow rate. A gas temperature above about 330°C is desirable because ammonium bisulfate tends to deposit on the catalyst at lower temperatures.

### 3.2 Combination of SCR and FGD

Figure 4 shows combined SCR-FGD systems for coal-fired boilers. The SCR reactor of the Shimonoseki unit (A) treats flue gas with a full dust load of about 20 $g/Nm^3$ (high-dust system). Those of the Tomato-Atsuma and Takehara units (B and C) treat the gases leaving a hot ESP containing less than 0.1 $g/Nm^3$ of dust (low-dust system). Both systems have been operated with neither erosion nor plugging of the catalyst by fly ash.

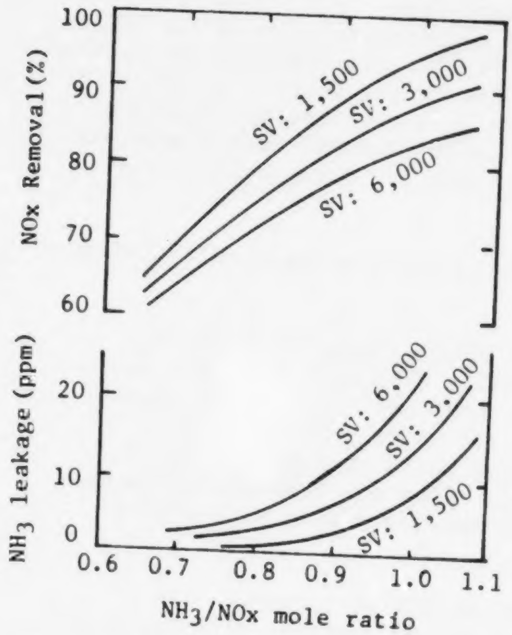


Figure 2 SCR for Coal-fired Boiler Flue Gas
(350°C, Honeycomb Catalyst)

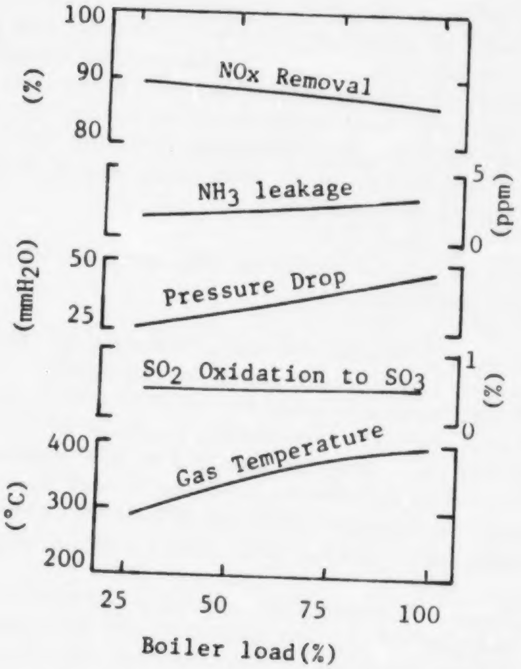
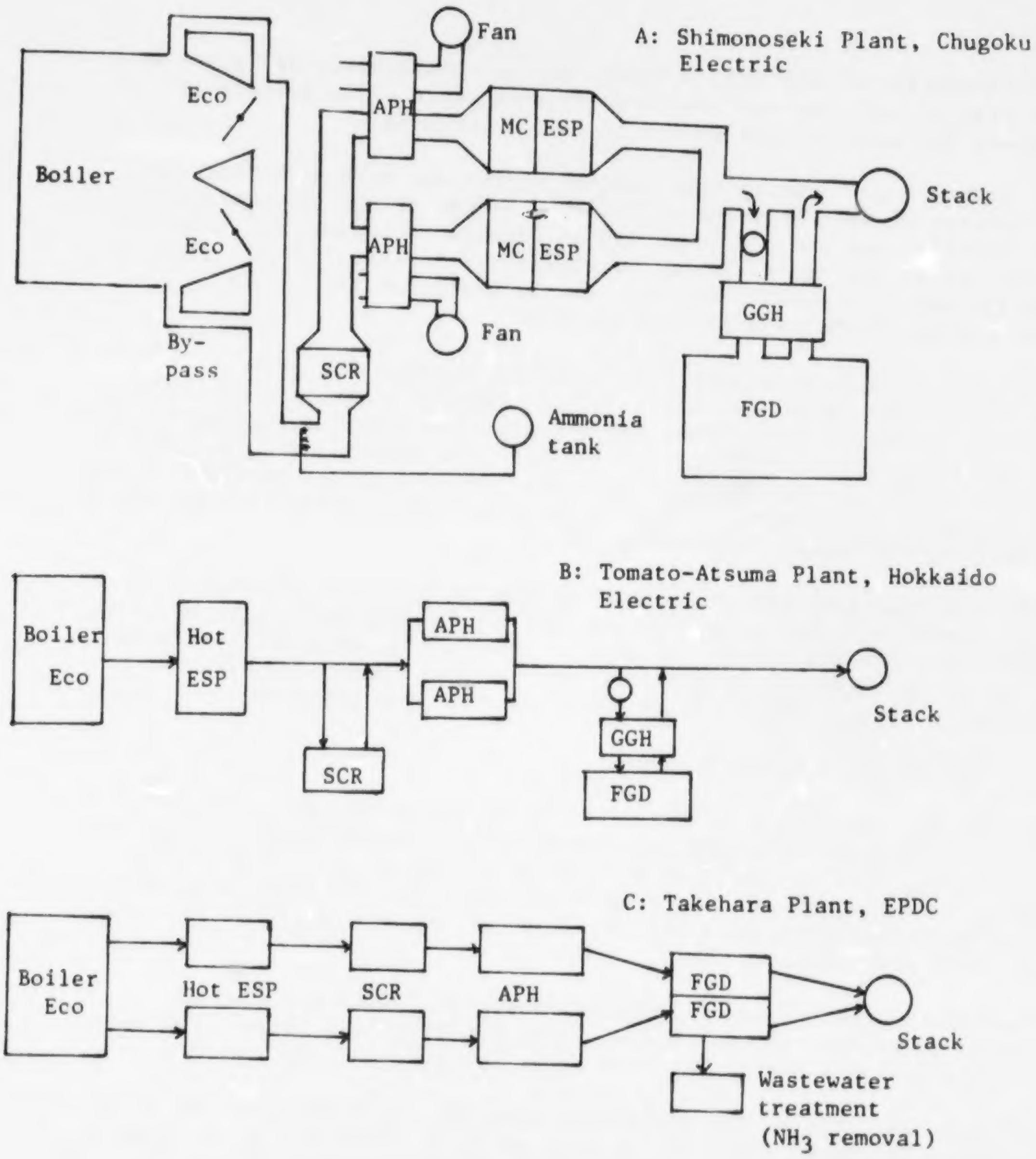


Figure 3 Boiler Load and Performance of SCR



Eco: Economizer APH: Air Preheater MC: Multi-cyclone

ESP: Electrostatic Precipitator GGH: Gas-gas Heat Exchanger

Figure 4 Combined SCR-FGD System in Operation for Coal-fired Boilers

The properties of fly ash, however, may be considerably different with the type of coal and the condition of combustion. The effects of various fly ashes on SCR should be further studied.

Hot ESPs are more costly than cold ESPs, but are more efficient for collection of dust from low-sulfur coal. Most of the SCR units under construction use the high-dust system because the deposit of ammonium bisulfate in the air preheater is eliminated by the cleaning effect of the fly ash, and because the dust can be sufficiently removed by the combination of the cold ESP and wet FGD.

SCR units usually give less than 5 ppm $NH_3$ leakage which is caught by wet FGD units. With Type I, II, or III FGD units, ammonia enters the scrubber system. The ammonia may not affect scrubber operation but may increase $SO_2$ removal efficiency.(2) With the Type IV unit, ammonia is caught by the prescrubber. In any case, ammonia at the scrubber outlet is virtually nonexistent; there is not the plume problem that is usually experienced at ammonia scrubbing FGD units.

With the high-dust system, a small amount of ammonia, 0.01-0.02% for 3-7 ppm ammonia leakage, may be contained in the fly ash caught by the cold ESP. The fly ash at Shimonoseki, where ammonia leakage is kept below 1 ppm, contains very little ammonia, and therefore gives no trouble when used as an additive to cement or for landfill.

## 3.3 Wastewater and Its Treatment

The pH and composition of wastewater from commercial FGD units for coal-fired boilers in Japan are shown in Table 6. The wastewater (from the prescrubber and scrubber) is treated with lime to precipitate heavy metals and fluoride which are filtered off. The filtrate is usually treated by ion exchange resin to remove dithionate $S_2O_6^{2-}$ which causes chemical oxygen demand (COD).

Usually the treated water contains below 10-15 mg/liter each of suspended solids and COD, below 15 ppm fluoride, and below 1 ppm oily material at pH 6.5-8.5. It thus satisfies existing regulations.

As shown in Table 6, the wastewater contains a considerable amount of nitrogen compounds which may be derived mainly from $NO_x$ in the flue gas. Flue gas from a coal-fired boiler usually contains 200-500 ppm $NO_x$. If 1-2% of the $NO_x$ is absorbed by the scrubbing liquor, the nitrogen content of the wastewater reaches 100-600 ppm as shown in Table 6, assuming that a 250 MW FGD unit purges 10 t/hr wastewater. So far, wastewater has not been treated to remove nitrogen compounds, because the total amount of nitrogen compounds is not much.

TABLE 6. pH AND COMPOSITION (mg/liter) OF WASTEWATER FROM FGD UNITS FOR COAL-FIRED BOILERS (BEFORE BEING TREATED)(1)

| | | |
|---|---|---|
| pH | 1 | 5 |
| Chemical oxygen demand | 30 | 100 |
| Suspended solids | 2,000 | 3,000 |
| Fluoride | 500 | 600 |
| Iron | 100 | 500 |
| Manganese | 10 | 30 |
| Magnesium | 200 | 1,000 |
| Aluminum | 100 | 1,400 |
| Chloride | 3,000 | 8,000 |
| Total Nitrogen[a] | 100 | 600 |

[a] Does not include ammonia derived from SCR of $NO_x$.

When SCR is applied upstream of FGD, ammonia is caught by the scrubber. Ammonia at a concentration of 5 ppm in flue gas from a 250 MW coal-fired boiler amounts to about 3 kg/hr. If the FGD unit for the boiler purges 10 t/hr of wastewater, the scrubber (or prescrubber) liquor as well as the wastewater may contain about 300 mg/liter of ammonia.

Adding lime causes much of the ammonia to be volatilized. If necessary, even more ammonia can be removed from the water. EPDC's demonstration plant at Takehara (combined SCR and Type II FGD) has a unit to remove ammonia from wastewater by a conventional activated sludge process; ammonia is reduced to 10 mg/liter. The Takehara plant faces the Seto Inland Sea which occasionally has a "red tide" problem. Therefore, reducing ammonia to a low level is desirable.

In Japan, a small amount of ammonia has been added to the flue gas from oil-fired utility boilers to neutralize sulfuric acid mists and to protect ESPs from corrosion. Thus ESP outlet gas usually contains about 5 ppm $NH_3$ which is caught by wet-process FGD and contained in the wastewater. At Chubu Electri's Owase-Mita plant, an ammonia stripping unit has been operated to reduce ammonia in FGD wastewater.(3)

When SCR is combined with a Type I FGD system, ammonia may be caught in the calcium sulfite slurry and may accumulate in the sludge pond when the supernatant is recycled to the scrubber. It may be necessary to minimize the ammonia emission from the SCR reactor.

It is likely that the nitrogen compounds shown in Table 6 will be reduced considerably by applying SCR and reducing $NO_x$ in flue gas. It may be possible that the total nitrogen compounds (including ammonia) may be lowered by applying SCR and keeping ammonia leakage at a very low level; e.g., 1 ppm or below at the Shimonoseki plant.

## 4. ECONOMICS OF FGD AND SCR

Investment costs of limestone-gypsum process FGD units for coal-fired boilers are listed in Table 7. The cost of the first units completed in 1975-1976, was 18,600 yen/kW.* The investment cost has since continued to increase mainly because of inflation. Chugoku Electric's Shimonoseki plant is fairly costly because it includes a Ljungstrom gas-gas heater to reheat the gas to 110-120°C. The gas-gas heater accounts for about 10% of the investment cost but, since it does not require fuel oil for gas heating, gives an overall economic advantage.

TABLE 7. INVESTMENT COST OF FGD UNITS FOR COAL-FIRED BOILERS (LIMESTONE-GYPSUM PROCESS, RETROFIT)

| Power company | Plant site | Capacity, MW | Investment cost | | Year completed |
|---|---|---|---|---|---|
| | | | $10^9$ yen | yen/kWhr | |
| EPDC | Takasago | 250 x 2 | 9.3 | 18,600 | 1975-1976 |
| EPDC | Isogo | 265 x 2 | 11.0 | 20,750 | 1976 |
| EPDC | Takehara | 250 | 7.2 | 28,800 | 1977 |
| Chugoku Electric | Shimonoseki | 175 | 7.0[a] | 40,000[a] | 1979 |

[a] Includes Ljungstrom gas-gas heat exchanger.

The estimated annualized FGD cost using a gas-gas heater for a 500 MW coal-fired boiler is about 1.9 yen/kWhr including 7 years depreciation. The fixed cost is 70% of the annualized cost.

Investment costs of SCR units for coal-fired boilers are shown in Table 8. As shown in Table 9, an SCR unit for a large new, coal-fired boiler costs 6,700-8,400 yen/kW for 80% $NO_x$ removal and about 30% more for 90% removal. An SCR unit for an existing boiler may cost 10-40% more. The annualized SCR cost is 0.6-0.8 yen/kWhr for 80% removal and nearly 30% more for 90% removal. Actually it is difficult to remove 90% of $NO_x$ with $NH_3$ leakage below 5 ppm for a large boiler because both gas flow rate and $NO_x$ concentration are not uniform in a large duct. Catalyst cost is over 60% of both investment and annualized costs.

---

*¥1 = $0.0043

TABLE 8. INVESTMENT COST OF SCR UNITS FOR COAL

| Station | Size (MW) | New (N) or Retrofit (R) | Constructor | Start-up | Cost (yen/kW) |
|---|---|---|---|---|---|
| Shimonoseki | 175 | R | MHI | 1980 | 9,700[a] |
| Tomato-Atsuma | 350x1/4 | N | BHK | 1980 | 10,000[b] |
| Takehara | 250x1/2 | R | BHK | 1981 | 7,000[b] |
| Takehara | 250x1/2 | R | KHI | 1981 | 8,000[b] |

[a] Including boiler modification for economizer by-pass.

[b] Approximation.

TABLE 9. ESTIMATED SCR COST FOR NEW 700 MW UTILITY BOILERS (Flue gas 2,300,000 $Nm^3/hr$. Annual power generation 4,292,400 MWhr. 70% utilization. $NH_3$ leakage less than 5 ppm. Honeycomb catalyst.)

| Fuel | High S coal | | High S coal | | Low S coal | |
|---|---|---|---|---|---|---|
| Inlet $SO_x$ (ppm) | 2500 | | 2500 | | 600 | |
| Inlet $NO_x$ (ppm) | 600 | | 300 | | 300 | |
| $NO_x$ removal (%) | 80 | 90 | 80 | 90 | 80 | 90 |
| Space velocity ($10^3$ $hr^{-1}$) | 2.2 | 1.6 | 2.7 | 2.0 | 3.0 | 2.2 |
| Investment cost[a] | | | | | | |
| $10^3$ yen/kW | 8.44 | 10.76 | 7.26 | 9.10 | 6.69 | 8.51 |
| U.S. \$/kW[b] | 36.7 | 46.8 | 31.6 | 39.6 | 29.1 | 37.0 |
| Annualized cost[c] | | | | | | |
| yen/kWhr | 0.81 | 1.04 | 0.65 | 0.82 | 0.59 | 0.76 |
| mill/kWhr | 3.5 | 4.5 | 2.8 | 3.6 | 2.6 | 3.3 |
| \$/lb of $NO_x$ removed[d] | 0.48 | 0.56 | 0.79 | 0.88 | 0.71 | 0.82 |

[a] Including initial charge of catalyst, civil engineering, and test operation. Catalyst: 3.5 x $10^6$ yen/$m^3$, 2 years life.

[b] \$1 = Y 230.

[c] Including 10% interest and 7 years depreciation.

[d] $NO_x$ calculated as $NO_2$ (1 lb = 0.45 kg).

A rough estimated cost for power generation is shown in Table 10. About 20% of the total investment for a coal-fired power station is for flue gas cleaning by FGD, SCR, and ESP. The investment cost of FGD is about 70% of the cost for flue gas cleaning. The estimated annualized cost of power generation with coal is 17 yen/kWhr, including nearly 3 yen for the flue gas cleaning. The cost is less than that with low-sulfur oil without flue gas cleaning.

TABLE 10. ESTIMATED POWER GENERATION COST (1981)

| | |
|---|---|
| Investment cost, yen/kW | |
| Coal-fired power station (excluding flue gas cleaning) | 200,000 |
| Flue gas desulfurization (90% efficiency) | 32,000 |
| Selective catalytic reduction (80% efficiency) | 7,000 |
| Electrostatic precipitator (99.5% efficiency) | 4,000 |
| Total | 243,000 |
| Annualized cost, yen/kWhr | |
| Flue gas desulfurization | 1.9 |
| Selective catalytic reduction | 0.6 |
| Electrostatic precipitator | 0.1 |
| Total power cost with coal including flue gas cleaning | 17.0 |
| Power cost with low-sulfur oil without flue gas cleaning | 20.0 |

## 5. SIMULTANEOUS $SO_x$ and $NO_x$ REMOVAL

### 5.1 Outline

Major simultaneous $SO_x$ and $NO_x$ removal processes are shown in Table 11. The copper oxide process has been applied to an oil-fired industrial boiler (40 MW equivalent).(4) Wet processes using $ClO_2$ or $O_3$ as the oxidizing agent and NaOH or $CaCO_3$ as the absorbent have been used for several gas sources (10-20 MW equivalent).(4) There is no plan for further application of those processes. The application of activated carbon and electron beam processes to coal-fired boilers has been studied. Wet processes using alkaline solutions containing EDTA and $FeSO_4$ to absorb $SO_2$ and NO have been tested but are not commercialized yet.

Pilot plant tests of fluidized-bed combustion (FBC) of coal (5 MW equivalent) are in progress at EPDC's Wakamatsu Station. Preliminary tests with domestic low-sulfur low-nitrogen coal indicated that $NO_x$ was lowered to about 60 ppm.(5) FBC, however, may not be used widely in Japan because of the difficulty in disposing of ash containing calcium compounds. Although tests are planned to use a synthetic absorbent which may be separated from fly ash for reuse, the method may not be practical.

TABLE 11. MAJOR SIMULTANEOUS $SO_x$ AND $NO_x$ REMOVAL PROCESSES

| Type | Absorbent, reagent | By-product |
|---|---|---|
| Dry process | Copper oxide, $NH_3$ | $N_2$ and S |
| | Activated carbon, $NH_3$ | $N_2$ and S |
| | Electron beam, $NH_3$ | $(NH_4)_2SO_4$ and $NH_4NO_3$ |
| Wet process | $ClO_2$, NaOH | $Na_2SO_2$, NaCl, and $NaNO_3$ |
| | $O_3$, $CaCO_3$ | $CaSO_4.2H_2O$, and $N_2$ or $NH_3$ |
| | $K_2SO_4$, EDTA, $FeSO_4$ | $N_2$ and S |

## 5.2 Activated Carbon Process(6)

Electric Power Development Co. (EPDC) and Sumitomo Heavy Industries (SHI) have conducted joint tests of the activated carbon process with a target of removing 95% of $SO_x$ and 40% of $NO_x$ in flue gas from a coal-fired boiler. A pilot plant with a capacity of treating 10,000 $Nm^3$/hr of flue gas from a coal-fired boiler at the EPDC's Takehara Station was operated from 1978 through 1980. The gas leaving an ESP at 120-150°C was added with 0.7 mol $NH_3$ to 1 mol $SO_x$ and was passed through a moving bed of activated carbon. Over 90% of $SO_x$ was adsorbed by the carbon with a space velocity of 500-900 $hr^{-1}$, while 20-40% of $NO_x$ was removed (Figure 5). The carbon was heated in a separate moving bed at 350°C by a hot inert gas to release concentrated $SO_2$. The carbon consumption was 0.5-1% per day.

The concentrated $SO_2$ was mixed with a small amount of air and introduced into a shaft furnace charged with anthracite coal or coke. By partial combustion in the furnace, gas temperature reached 900°C. About 90% of the $SO_2$ was reacted: about 45% to form elemental sulfur, 30% to form $H_2S$, and 10% to form COS. The gas, cooled to separate elemental sulfur by condensation, was led to three Claus furnaces in series to which a portion of the concentrated $SO_2$ was also added to react with $H_2S$ to form elemental sulfur. Thus 90% of the $SO_2$ recovered by the carbon was converted to elemental sulfur. The tail gas from the Claus furnace was incinerated and returned to the FGD system.

Ammonia played two roles: it reduced $NO_x$; and it reduced carbon consumption. The process may suit a flue gas with relatively low $SO_x$ content because the consumption of both ammonia and carbon decreases with $SO_x$ content. SHI claims that the process may compete with the wet limestone process for coal containing 1% or less sulfur. A demonstration plant with a capacity of treating 300,000 $Nm^3$/hr of flue gas from a coal-fired boiler will be constructed at EPDC's Matsushima Station in 1984.

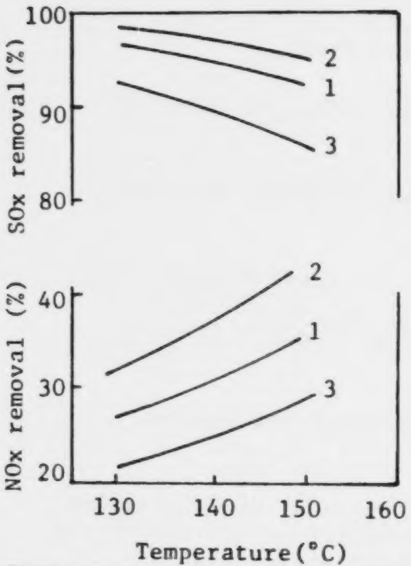
## 5.3 Electron Beam Process

Ebara Corporation and Japan Atomic Energy Research Institute have jointly developed a unique process to remove $SO_x$ and $NO_x$ simultaneously by electron beam radiation in the presence of ammonia. By the radiation, $SO_x$ and $NO_x$ form fine crystals of ammonium sulfate and nitrate, which are caught by an ESP or baghouse (fabric filter). The by-product is useful for fertilizer. A pilot plant with a capacity of treating 3,000-10,000 $Nm^3$/hr of flue gas from an iron-ore sintering machine was operated in 1978 (Figure 6).(7)

The process has been licensed to AVCO, U.S.A., which has tested the effects of coal fly ash on the process; the ash had no adverse effect on the process.(8) Over 70% removal of fly ash may be needed prior to the radiation to make the product useful for fertilizer. AVCO estimates that the investment cost is less than that for conventional wet lime scrubbing when a large size electron beam gun is used. Such a gun may be commercialized in the near future. Ebara estimates that the power consumption for treating flue gas from a coal-fired utility boiler is about 3% of the power generated by the boiler. The figure is a little larger than the consumption by the combination of SCR (0.1-0.2%) and FGD (2.0-2.5%). Although there are many simultaneous $SO_x/NO_x$ removal processes, the electron beam process may be the only process which may be useful in large-scale to recover $SO_x$, $NO_x$, and $NH_3$ as useful by-products.

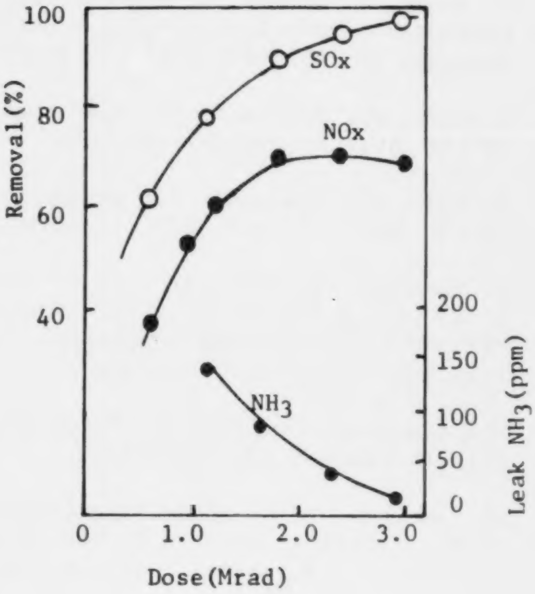
## 6. SUMMARY

Most coal-fired boilers in Japan are to use a flue gas cleaning system consisting of selective catalytic reduction (SCR) using a honeycomb or plate catalyst, electrostatic precipitators, and FGD by the limestone-gypsum process using a prescrubber with a separate liquor loop. The power generating cost by coal, including gas cleaning and wastewater treatment, is less than that by low-sulfur oil without gas cleaning. The fuel for several oil-fired boilers is to be changed to coal, using gas cleaning. However, the limestone-gypsum process is fairly costly. SCR is much less costly than FGD but is more costly than combustion modification (CM), and should be used with CM when CM alone is not sufficient to meet existing regulations. Simultaneous $SO_x/NO_x$ removal processes and fluidized-bed combustion have not yet been proved to be better alternatives to combined cleaning. Further development of $SO_x$ and $NO_x$ removal processes is desired.



| | Relative gas volume | Inlet (ppm) | |
|---|---|---|---|
| | | SOx | NOx |
| 1 | 100 | 910 | 230 |
| 2 | 80 | 910 | 170 |
| 3 | 120 | 910 | 200 |

Figure 5 Effects of Temperature and Gas Flow Rate on removal Efficiencies



Gas Flow: 3,000 $Nm^3$/hr

Temperature 90°C

Inlet Gas Composition
$SO_2$ 200 ppm, $NO_x$ 200 ppm
$NH_3$ 600 ppm

Figure 6 Test Results of Electron Beam Process

## LITERATURE CITED

1. The Panel on the Environmental Impacts of the Conversion to Coal, Environment Agency, An Analysis of the Environmental Impacts of the Expanded Use of Coal and Mitigation Measures--for the Proper Implementation of Environmental Impact Assessment (1981) (in Japanese).

2. G. Jones, R. Glover, G. Behrens, and T. Shirley, Impact of $NO_x$ Selective Catalytic Reduction Processes on Flue Gas Cleaning Systems, EPA/IERL-RTP-1287 (in print) (October 1981).

3. J. Ando, $SO_2$ Abatement for Stationary Sources in Japan, EPA-600/7-78-210 (NTIS PB 290198) (November 1978).

4. J. Ando, $NO_x$ Abatement for Stationary Sources in Japan, EPA-600/7-79-205 (NTIS PB 80-113673) (August 1979).

5. S. Tamanuki, H. Katayama, and N. Takami, 20 ton/h Pilot Plant Test of Fluidized Bed Boiler. In: Proceedings of the Third Coal Utilization Technology Symposium. Coal Mining Research Center (September 1981) (in Japanese).

6. Sumitomo Heavy Industries, Total Flue Gas Treatment by the Dry Desulfurization Process (1981).

7. K. Kawamura, Pilot Plant Experiment on the Treatment of Exhaust Gas from a Sintering Machine by Electron Beam Irradiation, Environmental Science and Technology, Vol. 14, No. 3, 288-293 (March 1980).

8. V. Shui and K. Kawamura, Removal of $SO_x$ and $NO_x$ from Flue Gases by Electron Radiation, 73rd Annual Meeting of APCA, Montreal (July 1980).

# EPA'S PILOT PLANT EVALUATIONS OF $NO_x$ AND $NO_x/SO_x$ FLUE GAS TREATMENT TECHNOLOGY

by: J. David Mobley
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Jack M. Burke
Radian Corporation
Austin, TX 78759

## ABSTRACT

Nitrogen oxide ($NO_x$) emissions from stationary sources may be reduced by 80 to 90 percent through the application of selective catalytic reduction (SCR) of $NO_x$ with ammonia ($NH_3$). For the most part, SCR has been developed and commercially applied in Japan. In the interest of evaluating SCR technology in the U.S., EPA has sponsored pilot-scale tests of two SCR systems treating flue gas from coal-fired boilers. The processes tested were the Hitachi Zosen process and the Shell Flue Gas Treatment (FGT) process, which also removes sulfur dioxide ($SO_2$). The results of those tests show that both processes tested are technically capable of reducing 90 percent of the $NO_x$ in flue gas which contains the full particulate concentration from a coal-fired boiler. A sampling program conducted during the pilot plant tests showed no adverse secondary emissions from application of the SCR processes; however, high $NH_3$ and sulfur trioxide ($SO_3$) emissions are a concern due to their potential for causing operational problems in downstream equipment. Cost projections, which are based on pilot plant results, show that the Hitachi Zosen process combined with a conventional flue gas desulfurization process is more cost effective and energy efficient that the Shell process for control of both $NO_x$ and $SO_2$ emissions.

## INTRODUCTION

In order to assess and promote the development of pollution control technology, EPA has sponsored research in many areas including flue gas desulfurization, particulate control, and combustion modifications. This research takes many forms ranging from theoretical studies to large-scale tests of new pollution control processes and techniques.

EPA's research activities have also addressed selective catalytic reduction (SCR) of nitrogen oxides ($NO_x$) with ammonia. As part of an effort to assess this technology in the United States, the EPA has sponsored pilot plant tests of two SCR processes. The processes tested were the Hitachi Zosen process and the Shell Flue Gas Treatment (FGT) process, which also removes $SO_2$. The tests were conducted using flue gas from two coal-fired boilers, and both pilot plants processed about 1600 $Nm^3/hr$ of flue gas which is equivalent to 0.5 MW of electric generating capacity.

The EPA-sponsored tests were the first of the Shell FGT process for $NO_x$ and $SO_2$ removal on a coal-fired boiler and the first coal-fired tests of the Hitachi Zosen process in the United States. Although the Hitachi Zosen process has been tested on coal in Japan, EPA felt that differences between the composition and properties of coals burned in Japan and those burned in the United States could affect the performance of the catalyst. As the results showed, fly ash properties at the United States test sites did affect operation of the Hitachi Zosen process, but did not impact operation of the Shell FGT process.

## OBJECTIVES

The SCR pilot plant tests had several objectives. The primary one was to document the ability of each process to treat flue gas from a coal-fired boiler. Other objectives included evaluation of the processes' ability to reduce $NO_x$ emissions by 90 percent for 90 days; measurement of emissions from the catalytic reactor of pollutants such as $NH_3$, $SO_3$, hydrocarbons, and CO; and measurement of the raw material and utility requirements of each process. Test programs were developed to meet these objectives, and the pilot plants were operated for nearly 2 years. During this period, several catalysts were tested over a wide range of operating conditions.

## PROCESS DESCRIPTIONS

### Hitachi Zosen (HZ) Process

The HZ process uses ammonia ($NH_3$), added to the flue gas, to selectively reduce $NO_x$ to molecular nitrogen ($N_2$) in a catalytic reactor. The overall chemical reactions are shown in Equations 1 and 2.

$$4\ NO(g) + 4\ NH_3(g) + O_2(g) \rightarrow 4\ N_2(g) + 6\ H_2O(g) \qquad (1)$$

$$2\ NO_2(g) + 4\ NH_3(g) + O_2(g) \rightarrow 3\ N_2(g) + 6\ H_2O(g) \qquad (2)$$

In the process, $NH_3$ is injected into flue gas which is at a temperature between 300°C and 400°C. The gas then passes through a catalytic reactor where the reduction reactions (Equations 1 and 2) occur rapidly.

The pilot test unit of the HZ process was located at Georgia Power Company's Plant Mitchell Station in Albany, Georgia. The HZ pilot plant processed a 1000-1500 scfm (1600-2400 $Nm^3/hr$) slipstream of flue gas which was withdrawn between the economizer and the air preheater of the coal-fired unit 3 at the Plant Mitchell Station. At this point, the flue gas contained the full particulate loading from the boiler. The slipstream from the boiler was first passed up through a flue gas heater for temperature control. $NH_3$ was then injected into the flue gas which flowed down through the reactor. After exiting the reactor, the gas passed through a cyclone particulate collector, a fan, and it then returned to the boiler flue gas duct. The particulate collector was included in the pilot unit to minimize abrasion in the fan.

## Shell Flue Gas Treatment Process

The Shell FGT process differs in that it removes both $SO_2$ and $NO_x$. Copper supported on alumina is used as an $SO_2$ "acceptor". $SO_2$ and $O_2$ react with the acceptor as shown in Equation 3.

$$SO_2(g) + \tfrac{1}{2}\,O_2(g) + CuO(s) \rightarrow CuSO_4(s) \qquad (3)$$

Copper oxide and, to a greater extent, the copper sulfate ($CuSO_4$) produced by the $SO_2$ acceptance reaction, act as a catalyst for the reduction of $NO_x$ by the injected $NH_3$ according to Equations 1 and 2.

As $SO_2$ is removed in the reactor, the acceptor becomes "loaded" and $SO_2$ emissions begin to increase. Once the time averaged $SO_2$ removal reaches the design level (e.g., 90 percent), flue gas flow to the reactor is shut off and the $CuSO_4/CuO$ are reconverted to Cu metal. In this regeneration step, a steam/hydrogen mixture is passed through the reactor and a concentrated $SO_2$ stream is produced. The regeneration reactions are illustrated by Equations 4 and 5.

$$CuSO_4(s) + H_2(g) \rightarrow CuO(s) + SO_2(g) + H_2O(g) \qquad (4)$$

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g) \qquad (5)$$

The $SO_2$ produced by the regeneration of the reactor can be further processed to recover the sulfur as sulfuric acid or elemental sulfur.

The Shell FGT pilot test unit was located at Tampa Electric Company's Big Bend Station in North Ruskin, Florida. The pilot plant processed a 1000 scfm (1600 $Nm^3/hr$) slipstream of flue gas which was withdrawn between the economizer and the air preheater of the coal-fired unit 2. Flue gas from the boiler contained full particulate loading and was heated by in-line burners before entering the reactor. Flue gas flowed up through the reactor during acceptance of $SO_2$ and bypassed the reactor during the regeneration of the acceptor. During the program, some tests were conducted in which the reactor was fully loaded with $SO_2$ and $NO_x$ was the only pollutant removed. While these tests were conducted, the reactor processed flue gas continuously.

## RESULTS[1,2]

The results of the pilot plant tests and subsequent data analysis can conveniently be divided into several categroies, including: process performance, process energy requirements, process costs, and the flue gas impacts of the process. When added together, these results are indicative of the technical and economic feasibility considerations of applying these two SCR processes to coal-fired boilers. In the discussion which follows, the pilot plant test results are summarized separately for each of these categories.

### Process Performance

The performance of the two pilot plants can best be summarized by the results of tests which were conducted to document the ability of the processes to reduce $NO_x$ emissions by 90 percent over 90 days of continuous operation. In the case of the Shell FGT process, simultaneous $SO_2$ removal efficiency of 90 percent was also required.

### Hitachi Zosen Process Performance--

The test results from the Hitachi Zosen pilot plant are presented in Figure 1. These results cover the period of May through October 1980, and represent over 3500 hours of operation. As illustrated by Figure 1, the Hitachi Zosen pilot plant met and exceeded the objectives of the test. During the first 90 days of operation, $NO_x$ removal averaged over 90 percent. And, for the entire period of 160 days of continuous operation, the average $NO_x$ reduction was 89.8 percent which is only slightly below the objective of 90 percent. Figure 1 also shows that in the range of 2100 to 2400 $Nm^3/hr$ flow rate has essentially no effect on the $NO_x$ removal efficiency of the process.

The results presented in Figure 1 indicate several things. They show that the Hitachi Zosen process is capable of treating flue gas from a coal-fired boiler for long periods of time while maintaining high $NO_x$ reduction efficiencies. But they also show that the activity of the catalyst gradually declined over the period May through October. This indicates that additional catalyst may be required to maintain 90 percent reduction over a 1 year period of operation. However, a catalyst regeneration technique was tested which may make it possible to maintain 90 percent $NO_x$ reduction without additional catalyst. Near the end of the test program, the NOXNON 600 catalyst was regenerated using an in situ, hot water washing technique. Following regeneration, the catalyst performance was essentially identical to that of fresh catalyst. Unfortunately, it was not possible to determine how long the effects of regeneration last or how many times the catalyst can be regenerated before a permanent loss of catalytic activity occurs. As a result, it is still uncertain if catalyst regeneration will permit the process to operate for 1 year at 90 percent $NO_x$ reduction efficiency without the use of additional catalyst.

The results presented in **Figure** 1 are for the Hitachi Zosen's NOXNON 600 series catalyst. Prior to testing the 600 series catalyst, the pilot plant tested the 500 series catalyst which has smaller openings for gas passage. During the tests, the NOXNON 500 catalyst became plugged with fly ash after about 2000 hours of operation. This was evidenced by an increase in reactor

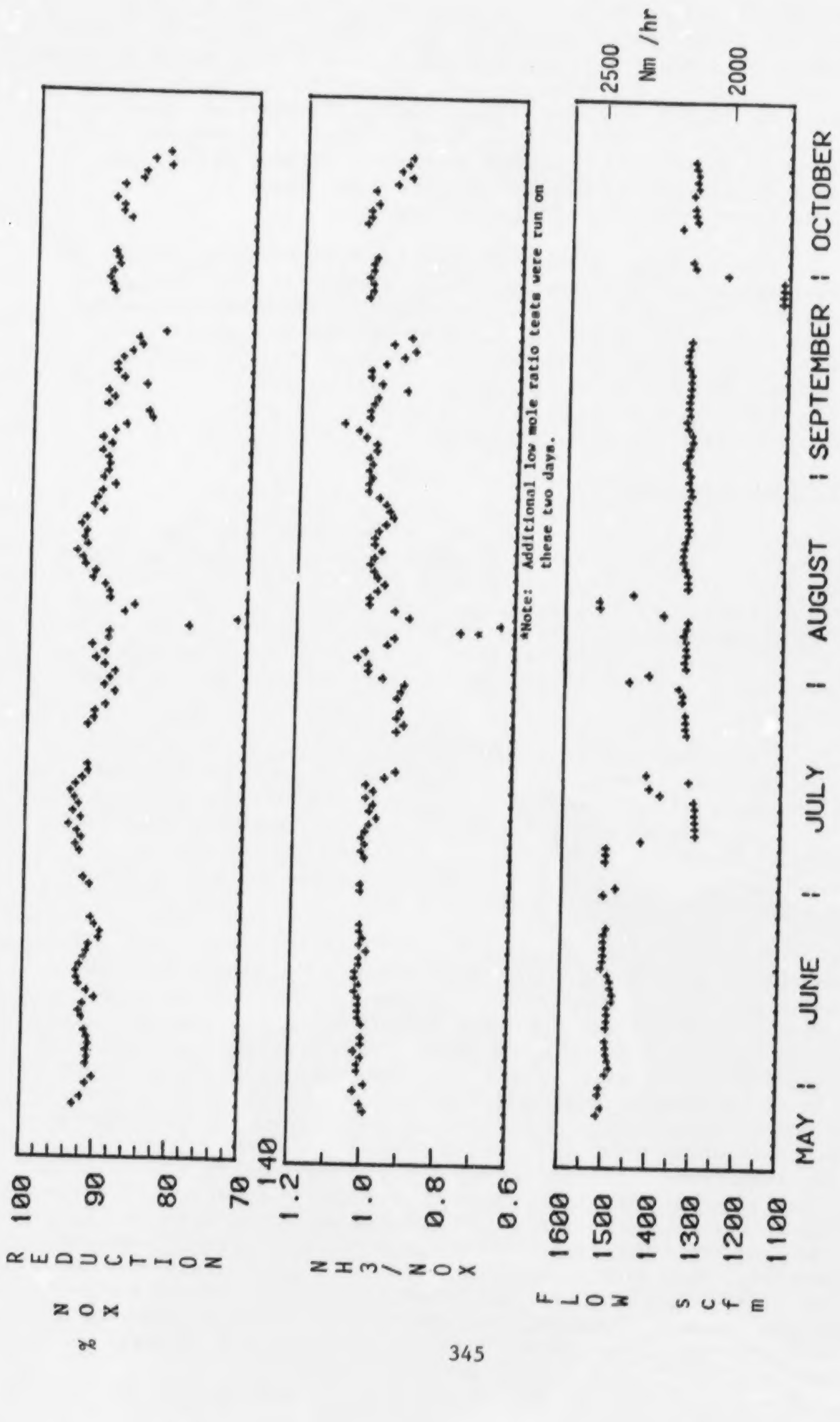


Figure 1. Pilot plant test results from the Hitachi Zosen process using $NH_3$ addition for $NO_x$ reduction.

pressure drop and a decline in $NO_x$ reduction efficiency, and it was believed to result from the adhesiveness of the fly ash at high temperatures. Tests were conducted which compared fly ash properties from a power plant in Japan with the properties of fly ash from the Plant Mitchell power plant in the United States. At reactor operating temperatures, fly ash from Japan remained as a fine powder but fly ash from Plant Mitchell agglomerated to form large lumps of material. This indicates a significant difference between a Japanese and United States coal-fired power plant and illustrates the need for test work in the United States.

In summary, the Hitachi Zosen tests indicated the need for a catalyst with larger gas passages to prevent catalyst plugging when treating flue gas from a coal-fired power plant in the United States. The tests did demonstrate that the process is capable of maintaining high $NO_x$ reduction efficiencies for long periods of time. And, although catalyst activity gradually declined during the test program, it may be possible to maintain 90 percent $NO_x$ reduction efficiency for a 1 year period with appropriate process design and operating considerations.

Shell FGT Process Performance--

The test results from the Shell FGT pilot plant are shown in Figure 2. These results are for tests conducted during June 1980, and they represent approximately 300 hours of operation in which flue gas was processed in the reactor. As Figure 2 illustrates, the Shell FGT process did not meet the objectives of the demonstration test. Although the $SO_2$ removal efficiency averaged 90 percent during the test, the $NO_x$ reduction averaged only 70 percent. And the test lasted only 20 days rather than the scheduled 90 days.

The inability of the pilot plant to meet the test objective of simultaneously reducing $NO_x$ and $SO_2$ emissions by 90 percent was due to the poor performance of the catalyst used in the process. With the reactor configuration used during the pilot plant tests, the $NO_x$ reduction efficiency was low even when $NH_3$ was injected to give an $NH_3$ to $NO_x$ ratio of 1.3. The $NO_x$ reduction efficiencies of the pilot plant could be improved, but only at the expense of reduced $SO_2$ removal.

The results of the tests at the Shell FGT pilot unit did not demonstrate **simultaneous** reduction of $NO_x$ and $SO_2$ emissions by 90 percent. However, the pilot plant test results can be extrapolated to identify conditions which will result in 90 percent reduction of both $NO_x$ and $SO_2$ emissions. To achieve this level of emissions reduction, additional catalyst would have to be added to the reactor. Under the conditions at the pilot plant test site, 50 to 75 percent additional catalyst would have been required. While addition of catalyst is technically feasible, it would significantly increase the costs of applying the process. (An alternative method of improving $NO_x$ reduction efficiency of the Shell FGT process was identified during the test program. The alternative method involved addition of processing steps to the $SO_2$ removal-$NO_x$ reduction cycle of the reactor. In a commercial design, the additional processing steps would require additonal process equipment. This evaluation of the Shell FGT process did not consider the alternative method since sufficient information was not available to enable a cost estimate; however, the reader should be aware that the alternative method may be less costly than use of additional acceptor in the reactor.)

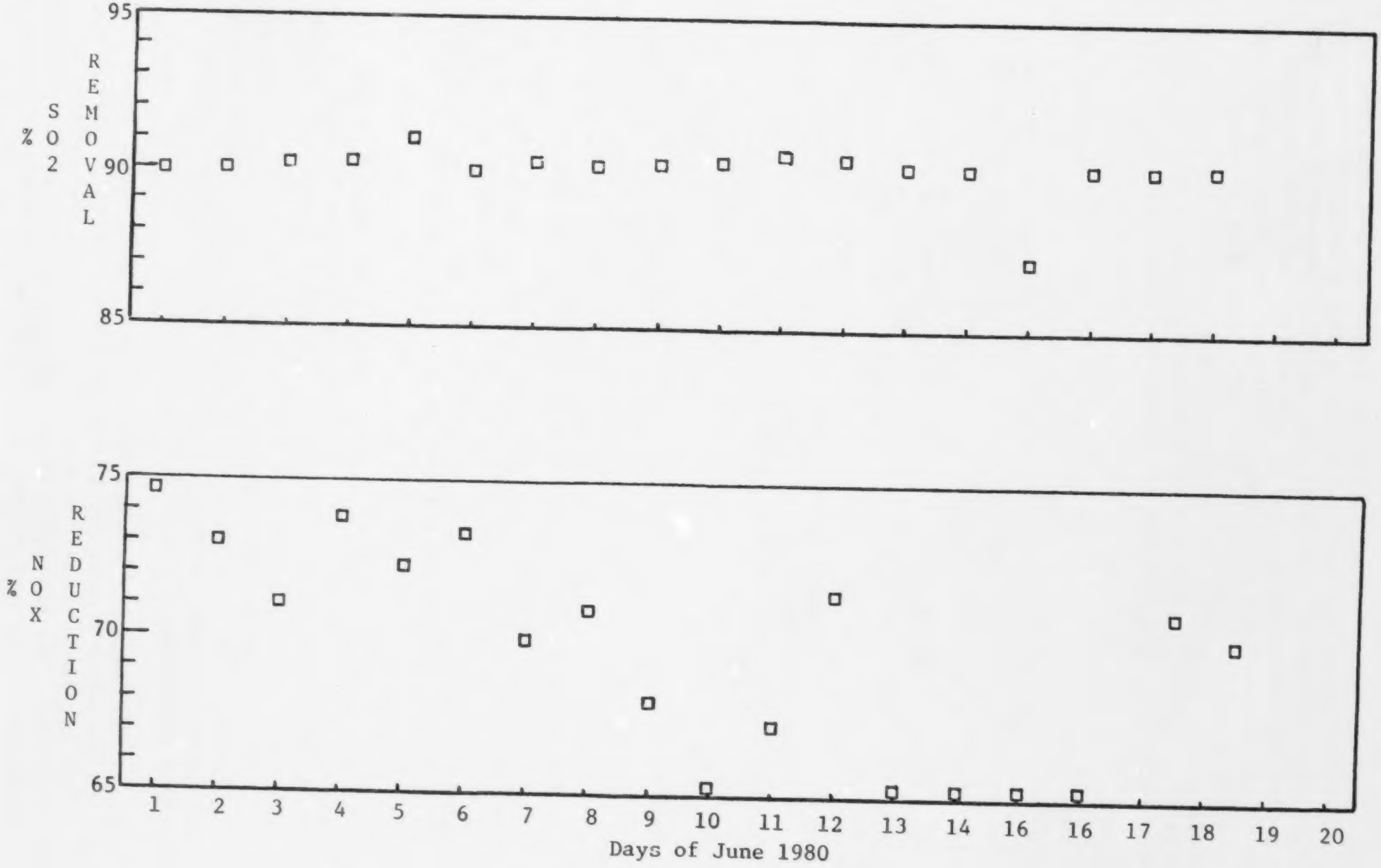


Figure 2. Pilot plant test results from the Shell Flue Gas Treatment process for $SO_2$, $NO_x$ removal from flue gas.

Another thing which was not attained during the tests with the Shell FGT process was the stability of the catalyst activity over a long period of time. Three catalysts were tested; of the three, the second processed flue gas for the longest period of time. Examination of the activity of this catalyst, as evidenced by its $SO_2$ removal efficiency, indicated that activity dropped after the catalyst's initial exposure to flue gas. The catalyst activity then stabilized and no measurable change in activity occurred over a 700 hour period. While this indicates that the catalyst activity appears stable for a coal-fired application, flue gas was not processed long enough to reach any conclusions.

Perhaps the most significant result of the tests with the Shell process was that no plugging of the reactor occurred. Flue gas was processed for a total of about 2000 hours and no increase in reactor pressure drop was recorded. This indicates that the parallel passage reactor design used in the pilot plant tests is well suited for application to coal-fired sources.

In summary, the tests of the Shell FGT process did not meet the objectives of the process to reduce emissions of both $NO_x$ and $SO_2$ by 90 percent. However, the results can be extrapolated to identify a process design which will reduce $NO_x$ and $SO_2$ emissions 90 percent. The test results did indicate that the parallel passage reactor design is well suited to coal-fired applications since no evidence of reactor plugging was found. But the test did not assess the long-term stability of the catalyst activity.

## Process Energy Requirements

One of the key factors used by the EPA in evaluating any pollution control process is the fraction of the boiler's output which is required to operate the pollution control system. This is a measure of how much of the boiler's capacity does not generate electricity for sale and is thus one factor which contributes to the costs of applying a pollution control process.

As part of an evaluation of the pilot plant test results, the energy requirements of both the Hitachi Zosen and the Shell FGT processes were estimated. These estimates were made for a 500 MW application of each process, and they were based on measurements made during the tests as well as estimates made in a previous study.(3)

Since the Shell FGT process reduces emissions of both $NO_x$ and $SO_2$ while the Hitachi Zosen process reduces only $NO_x$ emissions, a direct comparison of process energy requirements is not meaningful. Instead, energy requirements for the Hitachi Zosen process and energy requirements for a flue gas desulfurization process were estimated and compared with the energy requirements for the Shell FGT process. The results of these estimates are presented in Table I, which identifies individual components and the overall process energy requirements as a percentage of the boiler's capacity.

As Table I shows, the Shell FGT process has an energy requirement equivalent to 5 percent of the boiler's capacity while the Hitachi Zosen process combined with a flue gas desulfurization system required only 3.7 percent of the boiler's capacity. The principal difference between the energy demands of the two processes is the fuel energy requirement of the Shell FGT process.

TABLE I. COMPARISON OF HITACHI ZOSEN AND SHELL FLUE GAS TREATMENT PROCESS ENERGY REQUIREMENTS[a,b]

| Energy Component | Hitachi Zosen[c] | Shell |
|---|---|---|
| Fuel | - | 5.6 |
| Steam | 2.0 | 0.6 |
| Electricity | 2.0 | 2.0 |
| Energy Credit | (0.3) | (3.2) |
| Total | 3.7 | 5.0 |

[a] All energy requirements as percent of boiler capacity.

[b] 500 MW coal-fired boiler. Boiler thermal efficiency = 88%. Boiler heat rate = 9.5 MJ/kWh.

[c] Includes energy requirements for limestone flue gas desulfurization system.

The fuel energy consumed by the Shell process is equivalent to 5.6 percent of the boiler's capacity, and it is actually greater than the total process energy requirements. To some extent, the high fuel energy requirement of the Shell process is offset by the energy credit which results from application of the process. The energy credit is primarily the result of additional heat recovery in the air preheater due to lower permissible operating temperatures. Additional heat recovery is possible since samples collected during the pilot plant tests indicated that sulfur trioxide is removed from the flue gas in the reactor. This lowers the temperature at which sulfuric acid condenses (dew point), thus reducing the chance of corrosion in, or downstream of, the flue gas with lower preheater operating temperatures.

Another item of interest which is not shown in Table I is that the majority of the energy requirements shown for the Hitachi Zosen process are those of the flue gas desulfurization system: they are not associated directly with the SCR process. The estimated energy requirements of the Hitachi Zosen process alone are equivaelnt to only 0.3 percent of the boiler's capacity. These energy requirements result from compressed air and steam used for soot blowing and the electrical energy required to overcome the reactor pressure drop.

## Process Costs

Estimates were prepared of total capital investment and annual revenue requirements for the Hitachi Zosen process and the Shell FGT process based on results from the pilot plant tests and estimates from a previous study.(3) These costs reflect the way each process was operated during the pilot plant test program, and they can be used to compare the two processes. However, since the Hitachi Zosen process does not remove $SO_2$, the costs of a flue gas desulfurization system(3) must be added to the Hitachi Zosen process cost estimate to make comparison with the Shell FGT process costs meaningful.

Table II contains the results of the cost estimates for the Hitachi Zosen and Shell processes and the cost estimate for a limestone FGD system. As shown, the Shell process costs are estimated to be significantly higher than the costs for the Hitachi Zosen process, including the costs of flue gas desulfurization. The capital investment for the Shell process is estimated to be $84.2 million or $168/kW of generating capacity. The capital investment for the Hitachi Zosen process including FGD is estimated to be 72.5 million or $145/kW of generating capacity. This indicates that the capital investment of the Shell process is over 15 percent higher than that for the Hitachi Zosen process. The primary reason for the Shell FGT process's being more expensive is the relatively poor $NO_x$ reduction efficiencies attained by the process during the pilot plant tests.

TABLE II. ESTIMATED CAPITAL INVESTMENT AND ANNUAL REVENUE REQUIREMENTS FOR A 500 MW APPLICATION OF THE HITACHI ZOSEN AND SHELL FLUE GAS TREATMENT PROCESSES[a,b]

| Cost Item | Hitachi Zosen Process | | | Shell Process |
|---|---|---|---|---|
| | HZ | FGD | Total | |
| Capital Cost | $22,100,000 | $50,400,000 | $72,500,000 | $84,200,000 |
| Annual Revenue Requirement | 10,200,000 | 14,700,000 | 24,900,000 | 33,500,000 |

[a] A detailed breakdown of the Hitachi Zosen and Shell process cost estimates is included as an appendix to this paper.

[b] Basis for Estimates: 500 MW new coal-fired power plant burning 3.5 percent sulfur coal. 90 percent removal of both $NO_x$ and $SO_2$. Plant location in Midwestern United States. Project beginning mid-1977, ending mid-1980. Remaining life of power plant = 30 years. Plant on line 7000 hr/yr. Plant heat rate equals 9.5 MJ/kWh.

Perhaps a more important measure of relative process costs is the annual revenue requirements of the processes. The revenue requirements represent the annual costs of process operation including raw material and energy requirements, depreciation, return on investment, and catalyst replacement. These revenue requirements are also presented in Table II. It should be noted that these costs are based on the assumption of a 1 year life for the catalysts used in both processes. As discussed earlier, this assumption cannot be verified by the pilot plant test results, but a 1 year catalyst life is typically guaranteed by process vendors.

As shown in Table II, the annual revenue requirements for the Shell process are estimated to be $33.5 million/year. This is over 30 percent greater than the annual revenue requirements for the Hitachi Zosen process which were estimated to be $24.9 million/year. Again, the principal reason for the difference between the annual revenue requirements for the two processes is the relatively poor performance exhibited by the Shell process during the pilot plant tests which indicated that a substantial increase in catalyst volume would be required to achieve 90 percent $NO_x$ removal. Another significant difference is the relatively high energy requirements of the Shell process.

Overall, the results of the cost estimates indicate that the Shell FGT process requires a greater capital investment and has higher annual revenue requirements than the Hitachi Zosen process. However, the cost estimate was prepared only for a 500 MW coal-fired application with the requirements **of 90 percent $SO_2$ and $NO_x$ removal. The relative costs for the two processes could differ for other applications with different requirements.**

Process Flue Gas Impacts

As part of the pilot plant tests, EPA conducted a sampling program designed to quantify process emissions of pollutants other than $NO_x$ and $SO_2$. The objective of this sampling program was to determine if any adverse flue gas concentration impacts can result from application of SCR technology to a coal-fired source. Samples were collected at the inlet and outlet of the pilot plant reactors and analyzed for selected pollutants. Inlet and outlet samples were collected **simultaneously,** so that measured differences in pollutant concentration were due to changes across the reactors.

Table III identifies the specific pollutants measured and presents the results of the sampling program. As shown, the concentrations of some pollutants changed across the reactor while others did not. And in some cases, the concentrations of the pollutants were below the detection limits of the analytical techniques employed during the sampling program.

TABLE III. MEASURED CHANGE IN THE CONCENTRATIONS OF SELECTED POLLUTANTS ACROSS THE PILOT PLANT SCR REACTORS

| | Hitachi Zosen Pilot Plant | | Shell Flue Gas Treatment Pilot Plant | |
|---|---|---|---|---|
| Pollutant | Reactor Inlet Concentration | Reactor Outlet Concentration | Reactor Inlet Concentration | Reactor Outlet Concentration |
| Hydrogen Cyanide[a] | <10 $\mu g/m^3$ | <10 $\mu g/m^3$ | <10 $\mu g/m^3$ | <10 $\mu g/m^3$ |
| Nitrosoamines[a] | <5 $\mu g/m^3$ | <5 $\mu g/m^3$ | <5 $\mu g/m^3$ | <5 $\mu g/m^3$ |
| Carbon Monoxide | <0.017% | <0.017% | 0.13% | <0.017% |
| Hydrocarbons ($C_1$-$C_6$) | <1.0 ppmv | <1.0 ppmv | 28.5 ppmv | 21.0 ppmv |
| Sulfur Trioxide | 8.4 ppmv | 20.7 ppmv | 11.4 ppmv | 0.1 ppmv |
| Ammonia | 0 | 54.8 ppmv | 0 | 15.3 ppmv |

[a] **Gas volume taken at 15.5°C, 1 atm, dry basis.**

As illustrated in Table III, concentrations of hydrogen cyanide and nitrosoamines at the outlet of the pilot plant reactors were below the detection limits of the analytical techniques employed. For hydrogen **cyanide,** the detection limit is equivalent to 10 ppb and for nitrosoamines a maximum* of 2 ppb. In both cases, these concentrations are below the level which is considered safe for emissions from sources.

---

*The actual concentration level depends on the nitrosoamine compound(s) present.

At the Hitachi Zosen plant, the concentrations of both CO and hydrocarbons were also below the detection limits of the analytical techniques. But at the Shell FGT pilot plant, the concentrations of these compounds were found to decrease across the reactor. This decrease represents an environmental benefit for the Shell process, and it is believed to result from oxidation of these compounds in the reactor. It should be noted that the Hitachi Zosen reactor may also oxidize CO and hydrocarbons, but no conclusions can be drawn since those compounds were present in such low concentrations.

One of the most significant results of the emissions sampling program was the effect of the Hitachi Zosen and Shell processes on the concentration of $SO_3$ in the flue gas. As shown in Table III, $SO_3$ was produced in the Hitachi Zosen pilot plant reactor while the Shell FGT process removed $SO_3$ from the gas stream. These results are significant because of the effects of $SO_3$ can have on equipment located downstream of an SCR reactor, especially the air preheater.

In the case of the Hitachi Zosen process, the increased $SO_3$ concentration raises the sulfuric acid dew point of the flue gas. This increases the potential for formation of ammonium sulfates. The net effect of increased flue gas $SO_3$ concentrations is to increase process costs. This is reflected in the cost estimates of air preheater modifications which include provisions for soot blowing, water washing, and periodic replacement of the air preheater elements.

In the case of the Shell process, removing $SO_3$ reduces the sulfuric acid dew point of the flue gas. This permits the air preheater to operate at lower temperatures without experiencing corrosion in the preheater or in downstream equipment. The result is additional heat recovery which lowers process energy requirements and thus process costs. The low $SO_3$ concentration at the reactor outlet also minimizes the potential for formation of ammonium sulfates.

Another significant result of the emissions sampling program is the measured $NH_3$ emissions from the processes. As shown in Table III, $NH_3$ emissions from the Hitachi Zosen process were over three times greater than the emissions from the Shell FGT process even though the $NH_3/NO_x$ injection ratio was higher at the Shell pilot plant. This is due to the fact that the catalyst used in the Shell process promotes $NH_3$ oxidation while essentially no $NH_3$ oxidation occurred in the Hitachi Zosen process.

These results are significant since they indicate the potential for formation of ammonium sulfates downstream of the SCR reactors. Formation of ammonium sulfate is significant because it can result in corrosion and plugging of the air preheater and thus increase boiler operating costs. In the case of the Hitachi Zosen process, high $NH_3$ and $SO_3$ emissions indicate that a large quantity of ammonium sulfates can form downstream of the reactor. The Shell FGT process, on the other hand, has low emission rates of both $NH_3$ and $SO_3$. Thus, the potential for formation of ammonium sulfates is low.

## CONCLUSIONS

Several important conclusions can be drawn from the results of the pilot plant test program. First, and most important, the test results show that both the Hitachi Zosen $NO_x$ removal process and the Shell $NO_x/SO_x$ control process are technically capable of achieving significant reductions of $SO_2$ and $NO_x$ emissions from coal-fired boilers in the United States. Hitachi Zosen's NOXNON 600 catalyst and the Shell parallel passage reactor operated without fly ash plugging problems during the test program. The tests did show, however, that Hitachi Zosen's 500 series catalyst is prone to plugging. In contrast, tests by Hitachi Zosen in Japan reported that the NOXNON 500 catalyst treated flue gas from a coal-fired boiler for over 5000 hours without plugging problems. This difference between the properties of Japanese and United States coals points out the need for SCR test work when considering SCR process applications for untested coals.

In terms of performance, the Hitachi Zosen process met the test program objectives of 90 percent $NO_x$ reduction for 90 days while the Shell FGT process did not. The Shell process did not meet the test program objectives because the catalyst performance was below expected levels and therefore the pilot plant reactor was undersized.

The pilot plant tests did not demonstrate a 1 year catalyst life, but the Hitachi Zosen catalyst did process flue gas for 6 months while averaging nearly 90 percent $NO_x$ reduction. And although the Hitachi Zosen 600 series catalyst activity did decline during the test program, a regeneration technique was developed which restored catalyst activity to its original level. The performance of the Shell catalyst was quite stable during the test program, but the catalyst only processed flue gas for an equivalent of 3 months of operation. In both cases, a catalyst life of 1 year is typically guaranteed by the process vendors.

A comparison of the two processes, based on certain assumptions, shows that the Hitachi Zosen process combined with an FGD system has lower energy requirements and lower costs than the Shell FGT process. On the negative side, however, the Hitachi Zosen process has higher $NH_3$ and $SO_3$ emissions. Even so, it appears that the Hitachi Zosen process may be more cost effective than the Shell FGT process for a 500 MW boiler burning high sulfur coal. The pilot plant tests show that it may be possible to achieve highly efficient $NO_x$ and $NO_x/SO_x$ control by use of FGT technology on coal-fired sources in the United States. However, a prototype-scale test on a 10 to 100 MW facility may be necessary before the technology can be considered demonstrated for coal-fired sources in the United States.

## REFERENCES

1. J. M. Burke, Hitachi Zosen $NO_x$ Flue Gas Treatment Process; Vol. 2, Independent Evaluation, Radian Corporation, IERL-RTP-1337, January 1982, U.S. Environmental Protection Agency, Research Triangle Park, NC.

2. J. M. Burke, Shell Flue Gas Treating Process; Vol. 2, Independent Evaluation, Radian Corporation, Draft Final Report, January 1982, U.S. Environmental Protection Agency, Research Triangle Park, NC.

3. J. D. Maxwell, T. A. Burnett, and H. L. Faucett, Preliminary Economic Analysis of $NO_x$ Flue Gas Treatment Processes, Tennessee Valley Authority, EPA-600/7-80-021 (NTIS PB 80-176456), February 1980, U.S. Environmental Protection Agency, Research Triangle Park, NC.

# APPENDIX

## CAPITAL INVESTMENT AND ANNUAL REVENUE REQUIREMENTS FOR FULL SCALE SYSTEMS

### TABLE A-I. ESTIMATED CAPITAL INVESTMENT FOR A 500 MW APPLICATION OF THE SHELL FGT PROCESS[a]

| | Investment, $ | % of total direct investment |
|---|---|---|
| Direct Investment[b] | | |
| $NH_3$ storage and injection | 890,000 | 1.9 |
| $H_2SO_4$ plant | 7,172,000 | 15.2 |
| Reactor section | 27,455,000 | 58.1 |
| Flow smoothing section | 2,828,000 | 6.0 |
| Steam naphtha reformer | 4,698,000 | 9.9 |
| Gas handling | 1,546,000 | 3.3 |
| Sub-total direct investment (DI) | 44,589,000 | 94.4 |
| Services, utilities (0.06 x DI) | 2,675,000 | 5.6 |
| Total direct investment (TDI) | 47,264,000 | 100.0 |
| Indirect Investment | | |
| Engineering design and supervision | 709,000 | 1.5 |
| Architect and engineering contractor | 177,000 | 0.4 |
| Construction expense = $0.25\ (TDI \times 10^{-6})^{0.83}$ | 6,135,000 | 13.0 |
| Contractor fees = $0.096\ (TDI \times 10^{-6})^{0.76}$ | 1,799,000 | 3.8 |
| Total indirect investment (IDI) | 8,820,000 | 18.7 |
| Contingency = 0.2 (TDI + IDI) | 11,217,000 | 23.7 |
| Total fixed investment (TFI) | 67,301,000 | 142.4 |
| Other Capital Charges | | |
| Allowance for start-up and modifications = (0.1) (TFI) | 6,730,000 | 14.2 |
| Interest during construction = (0.12) (TFI) | 8,076,000 | 17.1 |
| Total depreciable investment | 82,107,000 | 173.7 |
| Land | 14,000 | - |
| Working Capital | 2,051,000 | 4.4 |
| TOTAL CAPITAL INVESTMENT | 84,172,000 | 178.1 |

---

[a] Basis: 500 MW new coal-fired power plant, 3.5% sulfur coal, 90% $NO_x$ removal, 90% $SO_2$ removal. Midwest plant location. Represents project beginning mid-1977, ending mid-1980. Average basis for scaling, mid-1979. Investment requirements for fly ash disposal excluded. Construction labor shortages with overtime pay incentive not considered.

[b] Each item of direct investment induces total equipment costs plus installation labor, and material costs for electrical, piping, ductwork, foundations, structural, instrumentation, and site preparation.

## TABLE A-II. ESTIMATED AVERAGE ANNUAL REVENUE REQUIREMENTS FOR A 500 MW APPLICATION OF THE SHELL FGT PROCESS[a]

| Item | Annual quantity | Unit cost($) | Annual cost($) | % of annual revenue required |
|---|---|---|---|---|
| Direct Costs | | | | |
| Raw materials | | | | |
| $NH_3$ | $7.875 \times 10^6$ kg | 0.165/kg | 1,299,500 | 3.88 |
| Naphtha | 39.773 $m^3$ | 132.1/$m^3$ | 5,254,000 | 15.69 |
| Catalyst | - | - | 12,600,300 | 37.63 |
| Reformer catalyst | - | - | 125,100 | 0.37 |
| Total raw materials | | | 19,278,900 | 57.57 |
| Conversion costs | | | | |
| Operating labor and supervision | 29,200 labor hrs | 12.50/ labor hr | 365,000 | 1.09 |
| Utilities | | | | |
| Naphtha | 9,943 $m^3$ | 132.1/$m^3$ | 1,313,500 | 3.92 |
| Steam | 179,900 GJ | -1.896/GJ | 341,200 | 1.02 |
| Process water | 8,078,000 $m^3$ | 0.01585/$m^3$ | 128,000 | 0.38 |
| Electricity | 68,859,000 kWh | 0.029 kWh | 1,996,900 | 5.96 |
| Heat credit | 1,047,500 GJ | -1.896/GJ | (1,986,000) | (5.93) |
| Maintenance | | | 1,891,000 | 5.65 |
| Analyses | 4,380 labor hrs | 17.00/labor hr | 74,500 | 0.22 |
| Total conversion costs | | | 4,124,100 | 12.31 |
| Total direct costs | | | 23,403,000 | 69.88 |
| Indirect Costs | | | | |
| Capital charges | | | | |
| Depreciation = (0.06)(total depreciable investment) | | | 4,926,400 | 14.71 |
| Average cost of capital = (0.086) (total capital investment) | | | 7,238,800 | 21.62 |
| Overheads | | | | |
| Plant = 0.5) (conversion costs minus utilities) | | | 1,165,300 | 3.48 |
| Adminstrative = (0.1) (operating labor costs) | | | 36,500 | 0.11 |
| Marketing = (0.1) (sales revenue) | | | 366,000 | 1.09 |
| Total indirect costs | | | 13,733,000 | 41.01 |
| Spent catalyst disposal | | | 11,400 | 0.03 |
| Gross average annual revenue requirement | | | 37,147,400 | 110.92 |
| Byproduct Sales Revenue | | | | |
| $H_2SO_4$ | 11.1x10 kg | -0.033/kg | (3,660,000) | (10.92) |
| TOTAL ANNUAL REVENUE REQUIREMENTS | | | 33,487,400 | 100.00 |

---

[a] Basis: 500 MW new coal-fired power plant 3.5% S coal. 90 percent $NO_x$ reduction, 90 percent $SO_2$ removal. Midwest power plant location, 1980 revenue requirements. Remaining life of power plant = 30 years. Plant on line 7000 hr/yr. Plant heat rate equals 9.5 GJ/kWh. Investment and revenue requirement for disposal of fly ash excluded. Total direct investment $47,264,000; total depreciable investment $82,107,000; and total capital investment $84,172,000.

## TABLE A-III. ESTIMAED CAPITAL INVESTMENT FOR A 500 MW APPLICATION OF THE HITACHI ZOSEN PROCESS[a]

| | Investment, $ | % of total direct investment |
|---|---|---|
| Direct Investment[b] | | |
| $NH_3$ storage and injection | 645,000 | 5.5 |
| Reactor section | 8,632,000 | 73.4 |
| Gas handling | 351,000 | 3.0 |
| Air preheater modifications | 1,461,000 | 12.4 |
| Sub-total direct investment (DI) | 11,089,000 | 94.3 |
| Services, utilities (0.06 x DI) | 665,000 | 5.7 |
| Total direct investment (TDI) | 11,754,000 | 100.0 |
| Indirect Investment | | |
| Engineering design and supervision | 274,000 | 2.3 |
| Architect and engineering contractor | 69,000 | 0.6 |
| Construction expense = 0.25 (TDI x $10^{-6}$)$^{0.83}$ | 1,933,000 | 16.4 |
| Contractor fees = 0.096 (TDI x $10^{-6}$)$^{0.76}$ | 625,000 | 5.3 |
| Total indirect investment (IDI) | 2,901,000 | 24.7 |
| Contingency = 0.2 (TDI + IDI) | 2,931,000 | 24.9 |
| Total fixed investment (TFI) | 17,586,000 | 149.6 |
| Other Capital Charges | | |
| Allowance for start-up and modifications = (0.1) (TFI) | 1,759,000 | 15.0 |
| Interest during construction = (0.12) (TFI) | 2,110,000 | 17.9 |
| Total depreciable investment | 21,455,000 | 182.5 |
| Land | 5,000 | - |
| Working capital | 336,000 | 2.9 |
| Royalty fee | 300,000 | 2.6 |
| TOTAL CAPITAL INVESTMENT | 22,096,000 | 188.0 |

[a] Basis: 500 MW new coal-fired power plant, 3.5% sulfur coal, 90% $NO_x$ removal. Midwest plant location. Represents project beginning mid-1977, ending mid-1980. Average basis for scaling, mid-1979. Investment requirements for fly ash disposal excluded. Construction labor shortages with overtime pay incentive not considered.

[b] Each item of direct investment includes total equipment costs plus installation labor, and material costs for electrical, piping, ductowrk, foundations, structural, instrumentation, insulation, and site preparation.

## TABLE A-IV. ESTIMATED AVERAGE ANNUAL REVENUE REQUIREMENTS FOR A 500 MW APPLICATION OF THE HITACHI ZOSEN PROCESS[a]

| Item | Annual quantity | Unit cost($) | Annual cost($) | % of annual revenue required |
|---|---|---|---|---|
| Direct Costs | | | | |
| Raw materials | | | | |
| NH | $5.25 \times 10^6$kg | 0.165/kg | 866,300 | 8.47 |
| Catalyst | | | 5,125,000 | 50.14 |
| Total raw materials | | | 5,991,300 | 58.61 |
| Conversion costs | | | | |
| Operating labor and supervision | 8,760 labor hrs | 12.50/ labor hr | 109,500 | 1.07 |
| Utilities | | | | |
| Steam | 86,700 GJ | 1.896/GJ | 164,400 | 1.61 |
| Electricity | 10,787,000 kWh | 0.029/kWh | 312,800 | 3.06 |
| Heat Credit | 92,400 GJ | -1.896/GJ | (175,200) | (1.71) |
| Maintenance = 0.04 x TDI | | | 470,200 | 4.60 |
| Analyses | 2,920 labor hrs | 17.00/ labor hr | 49,600 | 0.48 |
| Total conversion costs | | | 931,300 | 9.11 |
| Total direct costs | | | 6,922,600 | 67.72 |
| Indirect Costs | | | | |
| Capital charges | | | | |
| Depreciation = (0.06) (total depreciable investment) | | | 1,287,300 | 12.59 |
| Average cost of capital = (0.086) (total capital investment) | | | 1,900,300 | 8.59 |
| Overheads | | | | |
| Plant = (0.5) (conversion costs minus utilities) | | | 314,700 | 3.08 |
| Administrative = (0.1) (operating labor costs) | | | 11,000 | 0.11 |
| Total indirect costs | | | 3,513,300 | 34.37 |
| Spent catalyst disposal | | | (214,000) | (2.09) |
| TOTAL ANNUAL REVENUE REQUIREMENTS | | | 10,221,900 | 100.00 |

---

[a] Basis: 500 MW new coal-fired power plant, 3.5% S coal. 90 percent $NO_x$ reduction, 90 percent $SO_2$ removal. Midwest power plant location, 1980 revenue requirements. Remaining life of power plant = 30 years. Plant on line 7000 hr/yr. Plant heat rate equals 9.5 MJ/kWh. Investment and revenue requirement for disposal of fly ash excluded. Total direct investment $11,754,000; total depreciable investment $21,455,000; and total capital investment $22,096,000.

# DOE'S ELECTRON BEAM IRRADIATION DEVELOPMENTAL PROGRAM

By: Edward C. Trexler, P.E.
Program Manager
Flue Gas Cleanup
U.S. Department of Energy
Washington, DC 20545

## ABSTRACT

The Department of Energy's (DOE's) electron beam irradiation development program activities are conducted as part of the Advanced Environmental Control Technology (AECT) Program which is managed within the organization of the Assistant Secretary for Fossil Energy. The AECT program supports the development of cleanup systems to economically meet future emission limits so that the industrial and utility sectors can burn coal, which is abundant, rather than to burn premium fuels which are not. The electron beam (E-Beam) development program seeks to promote the development of systems for the simultaneous removal of $NO_x$, $SO_x$, and particulates from such flue gas streams. Electrons pass through a thin window into the flue gas causing the conversion of gaseous $NO_x$ and $SO_x$ into new sulfur and nitrogen particulate compounds which are then removed by conventional means.

The Primary R&D activities within DOE's program involve two jointly funded efforts with Avco-Everett/EBARA and Research-Cottrell. The High Voltage Engineering Corporation plays a prominent role as a subcontractor in both efforts. The Avco-Everett effort involves the testing of a configuration which utilizes ammonia injection upstream of the reactor and which produces a dry fertilizer by-product. The Research-Cottrell effort involves the testing of a configuration which utilizes a lime spray dryer upstream of the reactor and which produces a landfill waste product. An additional DOE E-Beam effort is being conducted at Florida State University where the use of electron irradiation for particulate precharing is being evaluated.

CONTENTS

Page

- Background 361
  - Program Objectives and Approach 361
  - Initial E-Beam Activities 361
- Flue Gas Electron Irradiation Phenomena 362
  - Configuration 362
  - Reaction Mechanisim 363
  - Preliminary Findings 365
  - Application Considerations 366
- Avco/EBARA (E-Beam/Ammonia) Process 366
- Research-Cottrell (E-Beam/Lime Slurry) Process 368
- Potential Benefits 370
- DOE R&D Plans/Actions 371
  - Research-Cottrell Process PDU 372
  - Avco/EBARA Process 372
  - E-Beam Kinetics 372
  - E-Beam Precharger 373
- Summary 373

# BACKGROUND

## Flue Gas Cleanup Program Objectives/Approach - 1982

The DOE Flue Gas Cleanup (FGC) Program like many other federal reserch and development (R&D) programs was reoriented in 1982 to place federal emphasis on the technology data base end of the spectrum rather than on the demonstration end. Accordingly, those FGD projects aimed at developing improved near term flue gas desulfurization (FGD) technologies were curtailed and attention was shifted toward the needs of the future. The program objective was focused on the development of simple and economic cleanup systems to meet the emission limits anticipated for the late 80's and 90's. The approach taken to meeting this objective was to emphasize combined $NO_x/SO_x$ removal technologies and in particular to seek out ways of removing both $NO_x$ and $SO_x$ in a single reactor. The electron irradiation processes were identified as potentially having those general qualifications.

Looking further at what might be reasonable emission limits for this period leads to the general conclusion that $NO_x$ control will probably receive increased attention. $NO_x$ emissions are believed to have deliterious effects on human health and visibility and are believed to be significant contributors to the formation of both nitrate and sulfate acid precipitation. $NO_x$ emissions from stationary sources have been steadily increasing while $SO_2$ and particulate emission have been leveling off or decreasing. Taking these factors into consideration, we therefore chose as interim R&D targets for this future period the following general emission specification:

$NO_x$ - 70 to 90% control level
$SO_2$ - Same level as now
Particulates - Same as now, but with further limits on respirable particles.

Further, as part of our specification for the future we would seek simple and economic systems which minimize the use of premium fuels and which produce either a useful or benign waste prooduct. The electron-irradiation technologies again would appear to qualify as candidates for meeting these specific goals.

## Initial E-Beam Activities

DOE's initial involvement in E-Beam $NO_x/SO_x$ control was accomplished in 1979-1980 by Research-Cottrell under a contract from Dr. Fred Witmer of DOE's EV office. The Research-Cottrell evaluation was performed with the assistance of Ion Physics Co. and included both bench scale testing and application analysis. The results of this effort projected the potential benefit of several E-Beam Configurations. The Research-Cottrell tests also included some tests with coal ash injection which were positive but it remains to be demonstrated that the process will function as expected on a real coal fired flue gas stream.

Earlier work on electron irradiation of flue gas was conducted by the EBARA Corp. of Japan beginning in 1970. EBARA's efforts included the construction and operation of a 3MWe pilot unit in 1977/78 for the simultaneous desulfurization/denitrification of a steel sintering plant flue gas. Bench scale evaluations have also been made by Avco/Everett beginning back in 1977.

The timing was such that further work seemed desirable on this promising process to evaluate its potential on coal fired flue gas streams at a time when DOE programmatic emphasis was shifted toward simultaneous $NO_x/SO_x$ removal.

## Flue Gas Electron Irradiation Phenomena

### Configuration

A simplified depiction of an Electron Beam Reactor applied to a coal fired combustion flue gas stream is shown in Figure 1.

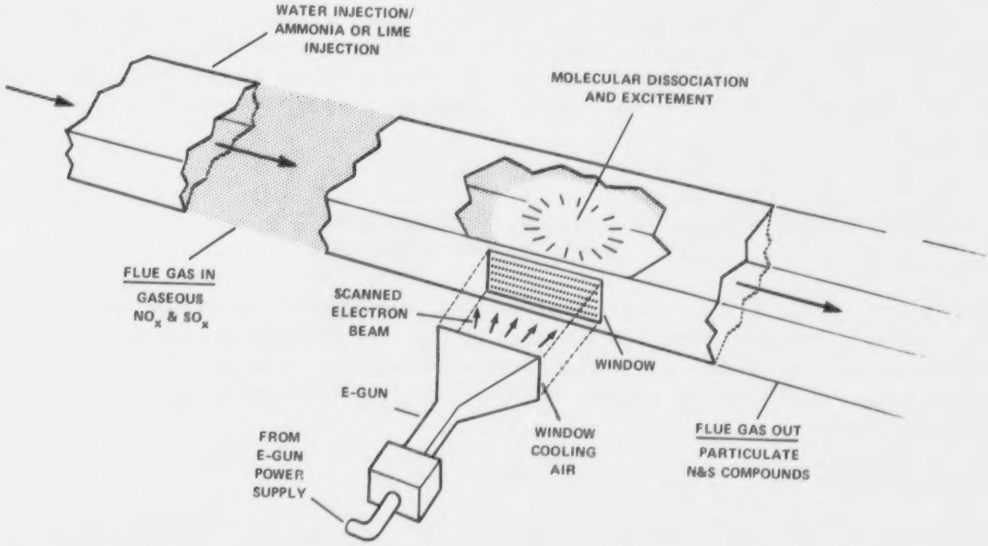


FIGURE 1 ELECTRON BEAM REACTOR

A commercial system would probably include an array of E-Guns and perhaps a centralized power supply serving several guns. A spray tower would be located upstream to the reactor and a particulate cleanup system would be located downstream.

A typical reactor section would consist of:

- A section of duct containing a thin foil window through which the electrons pass
- An electron gun with adequate voltage, capacity and scanning
- A central power supply for this E-Gun and perhaps others
- A means of cooling the foil windows
- Adequate shielding

Upstream to the reactor sections there would be a means of introducing water vapor into the flue gas streams. Other reactants such as ammonia or slaked lime might also be introduced depending on the process. Downstream from the reactor there would be a means for removing the particulate sulfates and nitrates from the gas stream.

Design features would be as follows:

The reactor duct would probably be made of stainless steel and would be designed and configured to promote efficient interaction with the electron spray.

The E-Guns would emply 600 to 800KV plates and would provide a continuous supply of electrons at a dose of 1 to 3 MRADs and would scan at about 200 cycles per second. (1MRAD = 10 Watt-Sec/Gram of Flue Gas)

A single power supply might power from four to eight guns.

The foil window used both in the duct and on the gun would be on the order of one to two thousands of an inch thick.

Windows would be cooled with filtered air augmented with a water cooled support grid.

Several feet of concrete might be needed for shielding or thicker sections of earth might be employed.

Water is introduced upstream to the reactor as necessary to achieve a sufficient concentration in the flue gas to cool the gas. Generally speaking, the higher the water content the better. There is a critical amount of water vapor which must be available in relationship to the $0_2$ available in the flue gas.

Reaction Mechanism

The reaction mechanism for the electron irradiation conversion of gaseous

$NO_x$ and $SO_x$ to particulate sulfates and nitrates is very complex and not fully understood.

A generalized description of the reaction is given by Figure 2 for the version of the process employing ammonia injection.

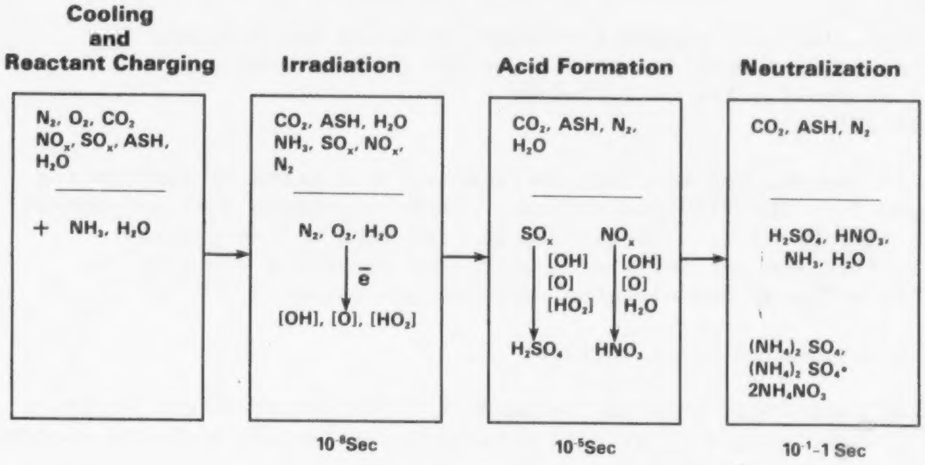


FIGURE 2 GENERALIZED REACTION CHEMISTRY
ELECTRON IRRADIATION WITH AMMONIA INJECTION

- Cooling and Reactant Charging Step

The gas containing $CO_2$. $N_2$, ash, $NO_x$, $SO_x$ and some $O_2$ and $H_2O$ is injected with water to cool the gas to 60-90°C and to bring the concentration of water above the critical amount. A near stoichimetric amount of ammonia is also injected in this version of the process.

- Irradiation Step

The cooled mixture is irradiated with electrons resulting in excitation and ionization and in the rapid formation of the radicals, HO, O, and $HO_2$.

- Acid Formation Step

These radicals then act to oxidize the $SO_x$ and $NO_x$ to sulfuric and nitric acid.

- Neutralization

Subsequent neutralization reactions take place between the acids, ammonia, and water vapor to form ammoniumsulfate $(NH_4)_2SO_4$ and ammoninium sulfate nitrate $(NH_4)_2SO_4NO_3$.

Readers interested in a more detailed treatment of the mechanism are referred to the work of Avco, EBARA and Research-Cottrell included in the references.

While a great deal of what we know about the process is empirical in nature, enough information has been gathered on the various forms of the process to begin to evolve the phenomenon into useful machines. Undoubtedly, as we learn more about the reaction mechanism we will be able to further optimize the process and create better and more economic processes.

Preliminary Findings

The following general empirical findings are evident from the studies and tests performed to date:

- Water injection up to the critical amount is necessary for proper reaction.
- Water must be present in a certain relationship to available oxygen. This critical amount is approximately 70% of the available oxygen.
- A modest amount of excess oxygen is necessary for proper reaction but excessive oxygen inhibits the reaction.
- Reaction is generally improved as gas temperature decreases to 60°C.
- Addition of ammonia enhances $SO_2$ capture and somewhat decreases $NO_x$ capture.
- Percent removal is independent of input concentration of $SO_x$ and $NO_x$.
- Ash slightly enhances the reaction.
- Percent removal increases with radiation.

Some of the quantitative results which can be deduced from the previous testing using simplified models to interpolate and extrapolate actual test results are as follows:

A - Systems Employing Water and Ammonia/Injection

- 10% moisture, 4% $O_2$, stoichiometric amount of $NH_3$
- 90°C
- capture as a function of irradiation:

|  | 1MRAD | 2MRAD |
|---|---|---|
| $NO_x$ capture | 50-80% | 60-90% |
| $SO_x$ capture | 80-85% | 90-92% |

### B - Systems Employing Water Injection Only

- 10% moisture addition, 4% $O_2$
- 60°C
- capture as a function of irradiation:

| | 1MRAD | 2MRAD | 3MRAD |
|---|---|---|---|
| $NO_x$ capture | 95% | 95-100% | 100% |
| $SO_x$ capture | 60-70% | 75-80% | 90% |

It is important to note from these results that significant opportunity exists to optimize the process either for maximum $SO_x$ or maximum $NO_x$ removal.

### Application Considerations

The following observations are important to the application of the phenomenon:

- Electron irradiation level input power needs are significant but tolerable:

| Dosage MRAD | EQUI. PWR. to Gas % of Plant | EQUI. PWR. @ 75% Eff. % of Plant | PWR. For 500 MWe Plant |
|---|---|---|---|
| 1.0 | 1.4 | 1.9 | 8.5 MWe |
| 1.5 | 2.0 | 2.7 | 14.0 MWe |
| 2.0 | 2.8 | 3.7 | 18.7 MWe |

- The economics of the process are strongly influenced by the capital cost of the E-Gun systems and where ammonia is used the relative cost of ammonia versus the sale price of the by-product as a fertilizer.

### AVCO/EBARA (E-Beam/Ammonia) Process

The AVCO/EBARA process is shown diagramatically in Figure 3. The process utilizes ammonia injection and produces a waste by-product of Ammonium Sulfate Nitrate which has significant value as a fertilizer. The selection of operating parameters such as gas temperature, oxygen, moisture and ammonia amount and the irradiation dosage are expected to fall within the range given for the previous generalized configuration.

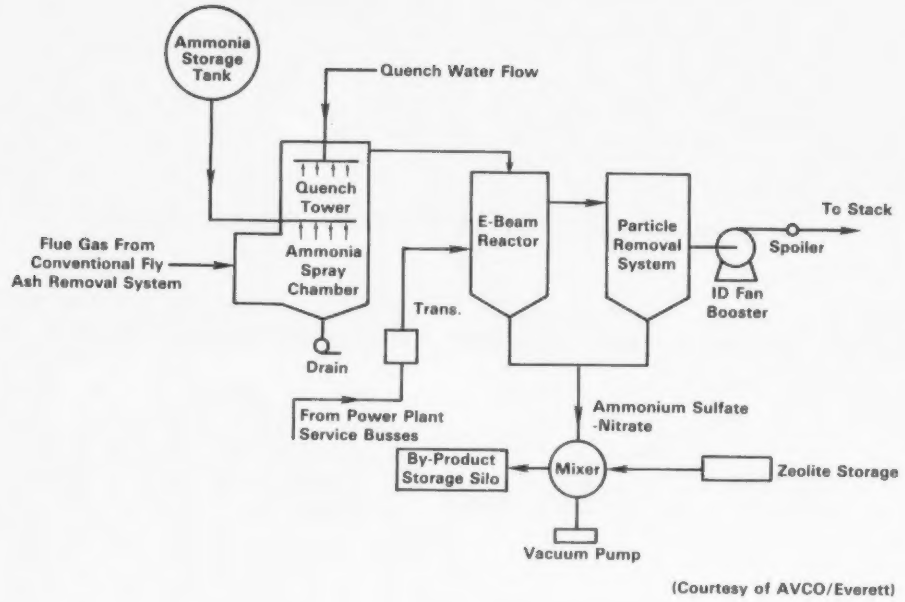


FIGURE 3 AVCO/EBARA (E-BEAM/AMMONIA) PROCESS – FLOW DIAGRAM

An artist depiction of a commerical unit employing several trains and an array of 150 KW E-Guns is given by Figure 4. The AVOC/EBARA process shows ash removal upstream of the reactor and ammonium sulfate nitrate particulate removal downstream.

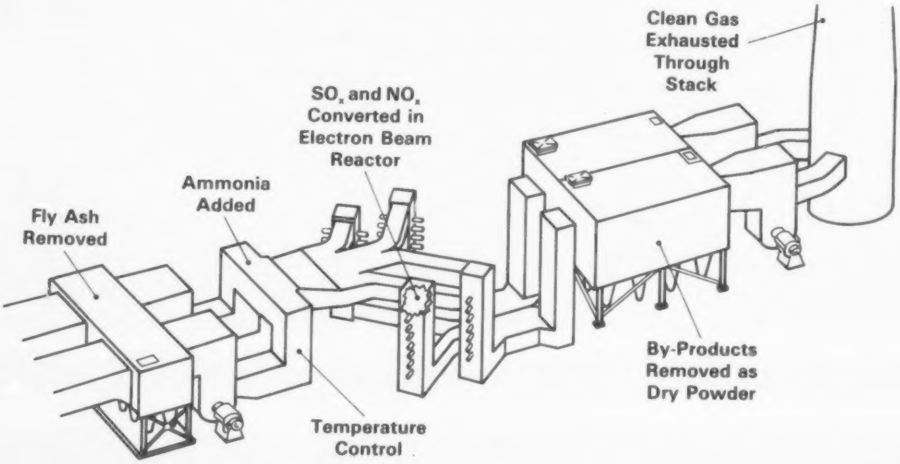
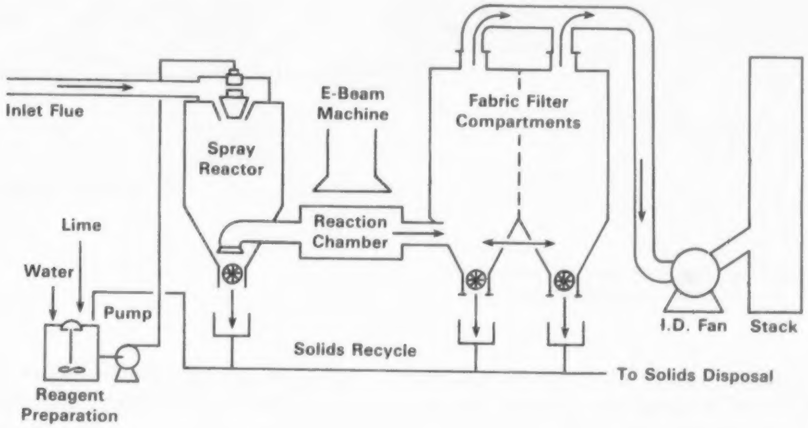

Clean Gas Exhausted Through Stack
$SO_x$ and $NO_x$ Converted in Electron Beam Reactor
Ammonia Added
Fly Ash Removed
By-Products Removed as Dry Powder
Temperature Control

FIGURE 4 AVCO/EBARA E-BEAM/AMMONIA COMMERCIAL CONCEPT

## Research-Cottrell (E-Beam/Lime Slurry) Process

The Research-Cottrell process couples an E-Beam reactor into a conventional spray dryer/baghouse system. A diagram of this process can be seen in Figure 5.



(Courtesy of Research-Cottrell)

FIGURE 5 RESEARCH-COTTRELL DRY SCRUBBER/E-BEAM SYSTEM

The spray dryer reactor replaces the ammonia/water spray tower used in the AVCO/EBARA system. $SO_2$ is removed in series with perhaps 60-70% being removed in the spray dryer followed by 65-75% of the balance being removed in the E-Beam reactor for an overall removal of around 90%

Both lime and electrons are conserved since both devices are used in the range of good utilization. This can be seen in Figure 6. A baghouse is used rather than an ESP in order to provide for further reaction of any residual acid mist in the filter cake. Waste products from the Research-Cottrell process consist primarily of $CaSO_4$, $Ca(NO_3)_2$, and ash which are further reacted with lime to form an impervious solid with minimal leaching.

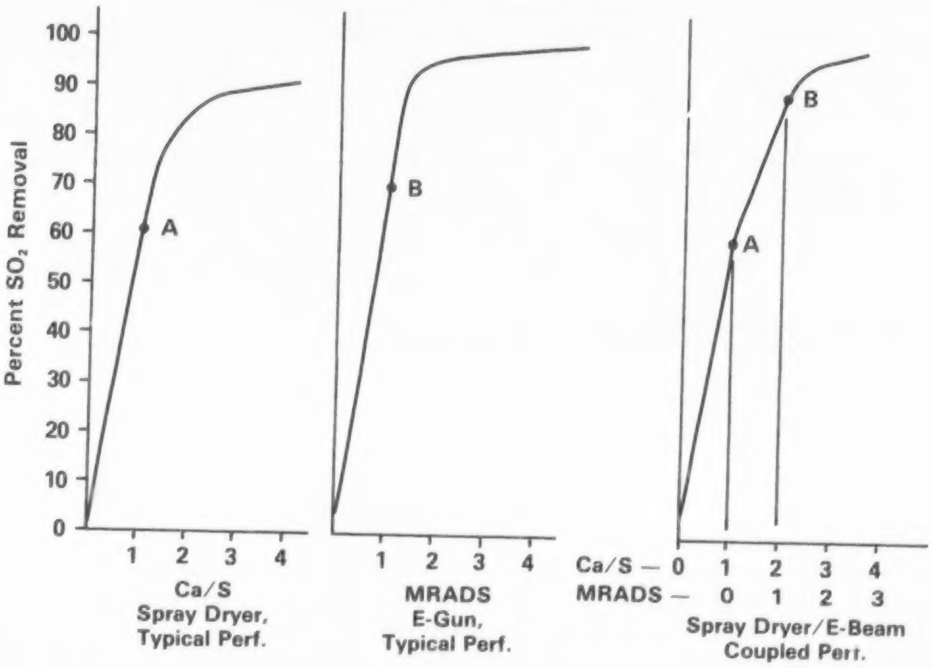


FIGURE 6 COUPLED PERFORMANCE E-BEAM AND SPRAY DRYER

The chemistry of the lime/slurry injection process differs from the ammonia injection process primarily in the "cooling and reactant charging" step and the "neutralization" step. The "cooling and activation" step, which now takes place in the spray dryer rather than in an ammonia/water spray tower, injects slaked lime rather than ammonia and includes a sulfation reaction where the lime reacts with some of the $SO_2$ to form calcium sulfite and calcium sulfate.

The "neutralization" step reacts the nitric and sulfuric acids with lime to form calcium sulfate and calcium nitrate. A generalization of these two modified steps is given in Figure 7.

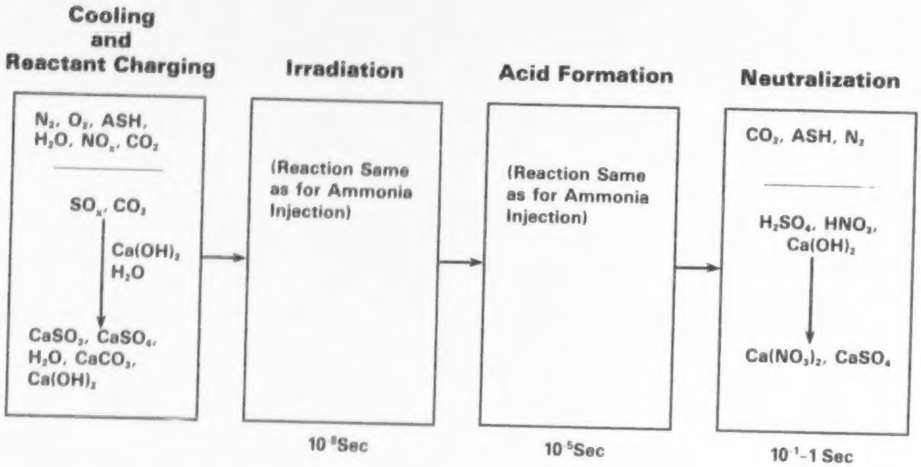

Cooling and Reactant Charging
Irradiation
Acid Formation
Neutralization
$N_2$, $O_2$, ASH, $H_2O$, $NO_x$, $CO_2$
$SO_x$, $CO_2$
$Ca(OH)_2$
$H_2O$
$CaSO_3$, $CaSO_4$, $H_2O$, $CaCO_3$, $Ca(OH)_2$
(Reaction Same as for Ammonia Injection)
(Reaction Same as for Ammonia Injection)
$CO_2$, ASH, $N_2$
$H_2SO_4$, $HNO_3$, $Ca(OH)_2$
$Ca(NO_3)_2$, $CaSO_4$
$10^{-8}$Sec
$10^{-5}$Sec
$10^{-1}$-1 Sec

FIGURE 7 GENERALIZED REACTION CHEMISTRY
ELECTRON IRRADIATION WITH LIME INJECTION

## Potential Benefits

Significant potential exists for incorporating the electron irradiation phenomina into useful flue gas cleanup systems for a number of applications. Economic analyses of conceptualized commerical systems employing both the ammonia injection and lime injection approaches show the potential for cost savings on the order of 20-25% over systems comprised of an L/L scrubber coupled with a selective catalytic reduction (SCR) system. The savings are expected to come primarily from:

- no expensive catalyst
- reduced gas handling needs because of lower pressure drops
- reduced reactor costs through the use of a simultaneous $NO_x/SO_x$ reactor
- reduced costs of handling the dry waste from the E-Beam system.

Cost savings of this level coupled with the projected significant increase in the use of coal for both the utilities and industrial sectors and the assumed degree of $NO_x$ and $SO_x$ control would result in savings to the economy on the order of $11 billion per year by 1990 and $21 billion per year by the year 2000.

These savings as noted before are strongly dependent on our ability to bring E-Gun systems costs down to the cost of $1.00 to 1.25 per watt of gun power which was assumed. The ammonia injection system is also sensitive to the relative cost of ammonia versus sale price of its fertilizer by-product.

As a word of caution, it is to be noted that the economic analyses which have been made to date are viewed as a guide in determining the propriety of engaging in further R&D and are lacking as the basis for judgement concerning commerical application. Meaningful analyses adequate for commerical application decisions must await the experience of building and operating process development units on real coal fired flue gas streams. In addition, exhaustive studies aimed at creating a new breed of low cost E-Gun systems for these applications would appear to be very much in order.

## DOE R&D Plans/Actions

The DOE program was aimed at providing a technology data base adequate to provide the basis for these more exhaustive analyses. The plan which involved (see Figure 8) and which was initiated in late FY 1981 called for proof-of-concept scale testing of both the ammonia injection and the lime slurry injection process on real coal fired slip streams and for certain associated studies. These additional efforts were to include E-Gun cost reduction and nitrate waste fixation studies aimed at answering questions important to the economics. In addition, these efforts were to be augmented with basic E-Beam kinetics tests aimed at more closely modeling the process and at assisting in optimization.

| E-Beam/Ammonia Process | E-Beam/Lime Process | E-Beam Kinetics | E-Beam Overview |
|---|---|---|---|
| • 10-20,000 SCFM PDU Slipstream | • 10,000 ACFM PDU Slipstream | • Bench Scale Tests and Modeling | • Independent Studies |
| • East H.S. Coal | • Typ. Coal | • 18 Months | |
| • Optimization Tests | • Optimization Tests | | |
| • Reliability Tests | • Nitrate Fixation Tests | | |
| • Fertilizer Studies | • E-Gun Cost Reduction Studies | | |
| • AVCO/EBARA | • Research-Cottrell | | |
| • Cost Share | • Cost Share | | |
| • 2 Years | • 2 Years | | |

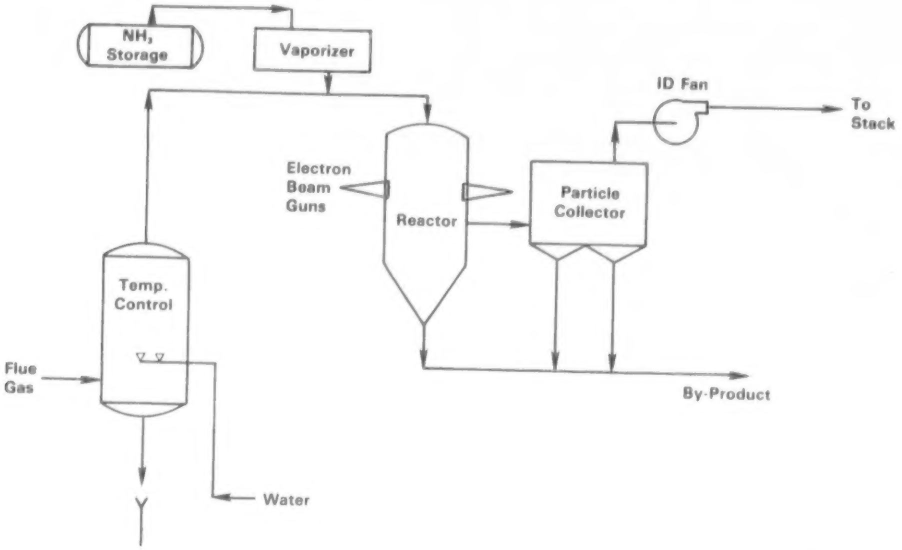
FIGURE 8 ELECTRON GUN $NO_x/SO_x$ FLUE GAS CLEANUP PROGRAM

### Research-Cottrell

A cost share cooperative agreement was signed in September 1981 with Research-Cottrell to evaluate the E-Beam/Lime Slurry process on a coal fired flue gas stream. A two year construction, test and study program is underway. Preliminary work has confirmed that a nitrate waste product from the process can be fixed adequately for landfill disposition and that off the shelf E-Beam components can be assembled today into what may be an economically competitive system. Agreements with a host site and subsequent commencement of construction is expected shortly.

### AVCO/EBARA

A contract was signed also in September 1981 with AVCO-Everett and with EBARA as a prime subcontractor for the preliminary design of a test scale E-Beam/Ammonia Injection system. It is anticipated that a cooperative agreement similar to the Research-Cottrell agreement will be concluded this year and that a similar two year program will be conducted. The proposed test unit is shown in Figure 9.



(Courtesy of AVCO-Everett)

FIGURE 9 AVCO/EBARA PDU PROCESS FLOW DIAGRAM

### E-Beam Kinetics

Under agreements reached within DOE the DOE-EV office (now part of DOE-EP) was to arrange for additional kinetics studies. This action has been delayed somewhat because of a lack of funds but it is expected to commence sometime during FY 1982.

## E-Beam Precharger

A related E-Beam effort has been underway for several years at Florida State University under the direction of Dr. Robert Davis aimed at exploring the potential use of the E-Beam in particulate cleanup. Copious supplies of ions can be created in flue gas with modest doses of electron irradiation and perhaps these supplies can be further enlarged through the use of an electric field. These findings lead to the possibility of creating a super precharger with E-Beam irradiation and perhaps the possibility of integrating particulate cleanup into the E-Beam $NO_x/SO_x$ reactor. A workshop was held in February of this year to explore these prospects.

## Summary

In summary it appears that there is a large potential benefit to be derived from the development and application of the E-Beam for flue gas cleanup. The E-Beam/Ammonia Injection process would appear to have its advantages in locations where there is a ready market for its fertilizer by-product. The E-Beam/Lime Slurry process would appear to look strong in other localities and where near 90% $NO_x$ capture is required. Both process variations would appear to have the potential for economic advantage over existing systems where higher levels of $NO_x$ control are required. The development of cheaper E-Gun systems is important to the economics of both processes. The experience of building and operating test units on real coal fired flue gas slip streams is necessary to provide a data base suitable for commerical application decisions. The DOE program is helping to provide this additional information.

# REFERENCES

1. Feldman, P.L. and Helfritch, D.J.; "The Research-Cottrell Dry Scrubber/E-Beam System, Particle Properties and Feasibility of E-Beam Precharging"; DOE E-Beam Particulate Control Workshop, February 25 and 26, 1982.

2. Gibbs & Hill Inc., "Avco/EBARA Flue Gas Treatment System Study", for Avco-Everett; April 1980.

3. Helfritch, D.J. and Feldman, P.L.; "The Removal of $SO_2$ and $NO_x$ from Flue Gas By Means of a Spray Dryer/Electron Beam Combination-A Feasibility Study"; CES-474, DOE E-Beam Particulate Control Workshop, February 25 and 26, 1982.

4. Kawamura, K. et al; "Pilot Plant Experiment on the Treatment of Exhaust Gas From a Sintering Machine by Electron Beam Irradiation"; Environmental Science and Technology, Vol. 14 P288-293, March 1980.

5. Research-Cottrell; "Removal of $NO_x$ and $SO_2$ from Flue Gas using Electron Beam Irradiation"; RPT. C00-4902-1, U.S Dept. of Energy, January 1980.

6. Slack, A.V. ; "Evaluation of the EBARA Process", RPT for EPRI, September 30, 1980.

7. Shui, Ven H.; "Avco/EBARA Electron-Beam Flue Gas Treatment System"; DOE E-Beam Particulate Control Workshop, February 25 and 26, 1982.

8. Trexler, E.C.; "Introductory Remarks at E-Beam Workshop on Combining Removal of $SO_x$/$NO_x$/Particulates", February 25 and 26, 1982.

9. TVA; "Economic Evaluation of Avco-EBARA Electron Beam Flue Gas Treatment Process"; November 1981.

## Session 6: LIMESTONE/ORGANIC ACID

J. David Mobley, Chairman
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

# BUFFER ADDITIVES FOR LIMESTONE SCRUBBING: A REVIEW OF R&D RESULTS

by: Gary T. Rochelle
Department of Chemical Engineering
University of Texas at Austin
Austin, TX 78712

## ABSTRACT

This paper reviews results on testing of buffer additives from laboratory to commercial-scale. Adipic acid at concentration levels of 2 to 20 mM (284 to 2840 ppm) substantially enhances the performance ($SO_2$ removal/$CaCO_3$ utilization) of slurry scrubbers with or without forced oxidation. Such enhancement can be used to increase $SO_2$ removal, increase limestone utilization, and/or reduce liquid-to-gas ratio (L/G). Other organic acids such as dibasic waste acid have been shown to be equally effective.

Organic acid makeup is required to replace losses resulting from solution entrainment in waste solids, coprecipitation in $CaSO_3$ solids, and oxidative degradation. Solution entrainment is minimized by dewatering waste solids; coprecipitation, by oxidation levels greater than 15%; and degradation, by lower pH with Mn present.

Adipic acid and its degradation products introduce insignificant levels of toxicity to waste solids and present no additional environmental problems.

The use of buffer additives adds a degree of freedom to scrubber operation that can be used to optimize cost while avoiding $CaSO_3$ scaling and other reliability problems.

## INTRODUCTION

Limestone slurry scrubbing is the dominant commercial technology for flue gas desulfurization. Additives that buffer between pH 3.0 and pH 5.5 enhance overall scrubber performance and can result in increased $SO_2$ removal, increased limestone utilization and reduced L/G. Flexibility from the use of buffer additives can permit improved reliability, use of limestone rather than lime, or use of higher-sulfur coal. This paper is a review of research and development results on the use of adipic acid (hexanedioic acid), waste dibasic acids (DBA), and other buffer additives.

Table 1 outlines the important milestones in the development and testing of buffer additives. Early work by Chemico (Villiers-Fisher and Warshaw, 1972) and TVA (Hatfield and Potts, 1972) on acetic and benzoic acids provided the impetus for a theoretical analysis of buffer alternatives by Rochelle

## TABLE 1: MILESTONES IN THE DEVELOPMENT OF BUFFER ADDITIVES

| Year | Event | References |
|---|---|---|
| 1969 | 1% Acetic Acid Enhances $SO_2$ Removal from 65 to 83% in lab scrubber | Villers-Fisher and Warshaw, 1972 |
| 1971 | 10 mM Benzoic acid enhances $SO_2$ removal from 50 to 75% in lab scrubber; adipic, glycolic, phthalic acids suggested | Hatfield and Potts, 1972 |
| 1973 | 10 mM Benzoic enhanced $SO_2$ removal in 2400 acfm pilot plant, turned pon red, 30% of acid unaccounted for | Holinden et al, 1974 |
| 1975 | Lab scale tests of adipic, citric, acetic | Wasag et al, 1975 |
| 1975 | Mass transfer theory recommends 5 to 10 mM buffer at $pK_a$ 4 to 5, adipic, sulfopropionic, sulfosuccinic recommended | Rochelle and King, 1977 |
| 1977 | Adipic acid demonstrated in 300 cfm pilot plant with forced oxidation and natural oxidation, valeric acid odor observed | Borgwardt, 1979 |
| 1978 | Adipic acid demonstrated in 10 MW prototype, material balance suggests unknown losses | Head et al, 1979 |
| 1979 | Conjugated oxidation identified as loss mechanism, valeric and glutaric found as degradation products | Meserole et al, 1979 |
|  | Degradation in 10 MW minimized by low pH | Burbank and Wang, 1981 |
|  | Mn identified as degradation inhibitor at low pH | Rochelle et al, 1982a |
| 1981 | Coprecipitation identified as additional loss mechanism, Ethane, Propane, butane observed as degradation products | Jarvis et al, 1982 |
|  | 4-carboxy-butanal identified as a degradation product | Rochelle et al, 1982b |
|  | DBA demonstrated at 300 cfm | Chang and Mobley, 1981 |
|  | Adipic and DBA demonstrated at 194 MW | Colley et al, 1982 |
|  | Adipic demonstrated in 20 MW industrial | Gerstle et al, 1982 |
|  | 70-day run in 10 MW, unknown degradation product observed | Wang and Burbank, 1981 |
| 1982 | DBA demonstrated with 50,000 ppm chloride | Chang and Laslo, 1982 |
|  | DBA commercially used at 194 MW | Hicks, 1982 |

(1977). He recommended EPA testing of adipic acid in the Research Triangle Park (0.1 MW) and Shawnee (10 MW) scrubber facilities. Pilot, prototype, and demonstration testing by EPA quantified the effectiveness of adipic acid and dibasic waste acid and identified problems of additive loss. Further laboratory and development work has resolved additive loss by degradation and coprecipitation.

Table 2 lists the R&D investigations by scale and performing organization. EPA-IERL has provided at least partial funding for all of the work except at Chemico and the University of California, the early theoretical work at the University of Texas, and the Radian/EPRI work with the Chiyoda process.

## PERFORMANCE TRADEOFFS

In limestone scrubbers, performance can be defined as the dependence of $SO_2$ removal on limestone utilization and scrubber L/G (or other variables such as $\Delta P$ which affect mass transfer capability). Buffer additives such as adipic acid enhance scrubber performance, resulting in increased $SO_2$ removal, increased limestone utilization, and/or reduced L/G.

Scrubber performance depends on the combined effects of $SO_2$ gas/liquid mass transfer, limestone dissolution, and $CaSO_3$ dissolution/crystallization. Theoretical work has successfully modeled the effects of buffers on $SO_2$ gas/liquid mass transfer and on limestone dissolution. However, integrated models of scrubber performance are still under development at the University of Texas and Radian Corporation.

Extensive testing in pilot plant and prototype scrubbers has quantified the effects of adipic acid and waste dibasic acids (DBA) on scrubber performance over a wide range of operating conditions and scrubber types.

### MECHANISMS

Scrubber performance is determined by the integrated effect of gas/liquid mass transfer, limestone dissolution, and $CaSO_3$ dissolution/crystallization. Buffer additives enhance $SO_2$ gas/liquid mass transfer by reducing the pH drop across the gas/liquid interface. They can also enhance the integrated effect of scrubber performance by reducing the pH drop from the scrubber inlet to scrubber outlet. Coincidentally, both of these effects require the same magnitude of buffer concentration.

The rate of $SO_2$ gas/liquid mass transfer in a limestone slurry scrubber is usually controlled by diffusion in both the gas and liquid films. Diffusion of $SO_2$ in the liquid film is enhanced by the equilibrium reaction giving $H^+$ and bisulfite ($HSO_3^-$):

$$SO_2(aq) + H_2O \rightleftarrows H^+ + HSO_3^-$$

To the extent that this reaction occurs, $SO_2$ can diffuse as both aqueous $SO_2$ and $HSO_3^-$. The equilibrium pH at the gas/liquid interface is typically 3 to 4 ($10^{-3}$ to $10^{-4}$ M $H^+$). The extent of the dissociation reaction is usually limited by diffusion of the $10^{-3}$ to $10^{-4}$ M $H^+$ from the gas/liquid interface to

## TABLE 2: SCOPE OF INVESTIGATIONS ON BUFFER ADDITIVES

### Theory

University of California - Berkeley (Rochelle, 1977; Rochelle and King, 1977; Rochelle and King, 1978)

University of Texas at Austin (Chang, 1979; Chang and Rochelle, 1982)

### Laboratory Studies

Chemico (G.E. Environmental Services)
    Scrubber Test Acetic (Villiers-Fisher and Warshaw, 1972)

Tennessee Valley Authority
    Alternatives/Scrubber Test Benzoic (Hatfield and Potts, 1972; Hatfield et al, 1974)

University of Texas at Austin (Rochelle et al, 1982a; 1982b)
    Mass Transfer (Weems, 1981; Chang and Rochelle, 1982)
    Buffer Alternatives (Cavanaugh, 1978; Smith, 1981)
    Degradation (Garcia, 1980; Hsiang, 1981)

Radian
    Degradation (Meserole, 1979; Meserole et al, 1979; Meserole et al, 1980; Terry et al, 1981; Jarvis et al, 1982)
    Chiyoda Thoroughbred 121-Adipic/EPRI (Behrens and Delleney, 1981)

### Pilot Plant

Tennessee Valley Authority
    Benzoic, 1 MW (Hollinden et al, 1974)

EPA/Acurex
    Adipic, 0.1 MW (Borgwardt, 1979; Chang, 1980)
    DBA, 0.1 MW (Mobley and Chang, 1981; Chang and Dempsey, 1982)
    DBA, high chloride, 0.1 MW (Chang and Laslo, 1982)

### Prototype

Bechtel/TVA
    Adipic, 10 MW, Natural and forced Oxidation (Head et al, 1979; Burbank and Wang, 1979; 1981; 1982; Wang and Burbank, 1981)

### Demonstration

Radian/Springfield
    Adipic/DBA, 194 MW (Hicks et al, 1981; Hargrove et al, 1981, Colley et al, 1982; Hargrove et al, 1982)
Pedco/Rickenbacker
    Adipic, 20 MW Industrial (Gerstle et al, 1981; Clarke et al, 1982)

bulk solution where the pH is typically 4.5 to 5.5.

An additive that buffers between the pH of the gas/liquid interface and the pH of the bulk solution will enhance $H^+$ diffusion and thereby increase diffusion of $SO_2$ as $HSO_3^-$. The basic buffer species ($A^-$) will diffuse from the bulk solution to the gas/liquid interface where it will react reversibly with $H^+$ to give the acid species (HA):

$$A^- + H^+ \rightleftarrows HA$$

$$pK_a = -\log \frac{[H^+][A^-]}{[HA]}$$

The acid species will diffuse back to be bulk solution and effectively carry a $H^+$ with it. For maximum effectiveness the buffer $pK_a$ value should be between the interface pH and the bulk solution pH. This mechanism can also be viewed as the overall equilibrium reaction of buffer species with $SO_2$ to generate additional $HSO_3^-$ at the gas/liquid interface:

$$A^- + SO_2(aq) + H_2O \rightleftarrows HA + HSO_3^-$$

Buffers also enhance integrated scrubber performance by reducing the amount of $CaCO_3$ or $CaSO_3$ that must dissolve in the scrubber to avoid a dramatic drop in pH as $SO_2$ is absorbed. To be effective in this manner the additive should buffer between the pH of the scrubber inlet solution (5.0-5.5) and the pH of the scrubber outlet solution (3.5-5.0). Over this pH range the additive should provide buffer capacity equivalent to the $SO_2$ make-per-pass, typically 5-15 mM for high-sulfur coal. Therefore 3 to 20 mM adipic acid could have a substantial effect on integrated scrubber performance. This effect will be most significant in systems with low concentrations of $CaSO_3$ and excess $CaCO_3$ solids, for example with forced oxidation in the scrubber loop at pH less than 5.

There is no net diffusion or consumption of buffer species. The basic species is regenerated in the bulk solution by dissolution of $CaCO_3$ or other alkaline solids in the scrubber or in the hold tank:

$$CaCO_3 + 2HA \rightarrow 2A^- + Ca^{++} + CO_2 + H_2O$$

## THEORETICAL RESULTS

The calculated effect of adipic acid on $SO_2$ gas/liquid mass transfer at a single gas and liquid composition is shown in Figure 1. These calculations account for both gas and liquid film resistance and use an approximation to the surface renewal model with multiple equilibrium reactions and unequal diffusivities (Chang, 1979). The ratio of the overall mass transfer coefficient ($K_g$) to the gas film mass transfer coefficient ($k_g$) is given as a function of adipic acid concentration. This ratio represents the fraction of mass transfer resistance in the gas phase and is inversely proportional to the required mass transfer capability of the absorber.

At sufficiently high values of adipic acid, $K_g/k_g$ approaches 1.0 and

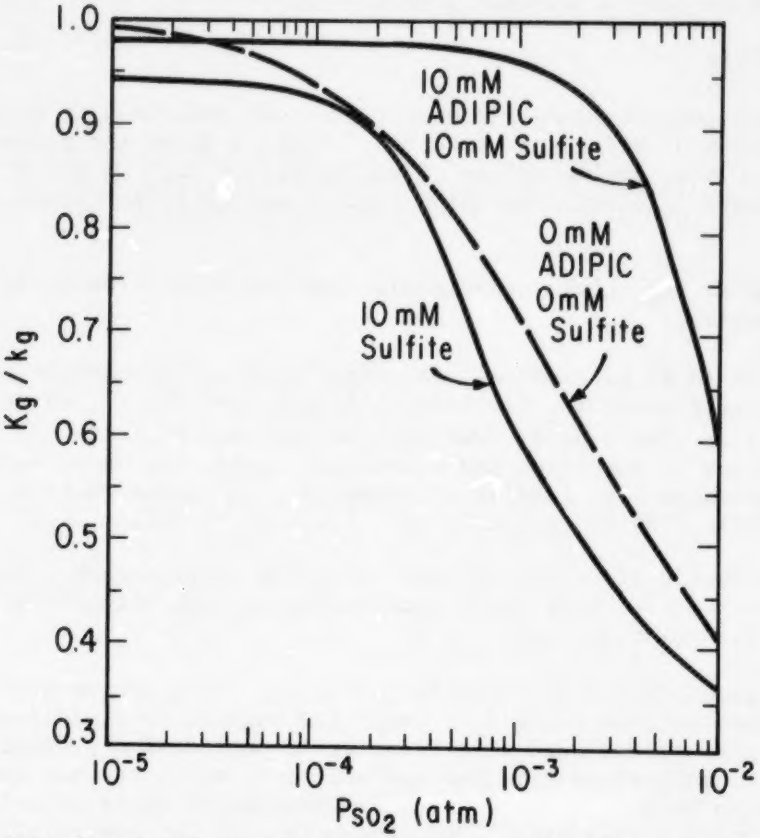


Figure 1. Calculated Effect of Adipic Acid on the Overall Gas Phase Mass Transfer Coefficient, pH 5, 55°C, 0.1 M $CaCl_2$, 0.12 atm $CO_2$, $k_l^{\circ}/k_g$=0.2 atm/M.

adipic acid has no more incremental effect. With 2000 ppm $SO_2$ and 10 mM total sulfite, 10 mM (1460 ppm) adipic acid is sufficient to get near the maximum effect of enhancing $K_g/k_g$ from 0.51 to 0.94.

At lower values of $SO_2$ partial pressure, gas-film resistance is more significant. Therefore, the maximum effect of adipic acid with 500 ppm $SO_2$ enhances $K_g/k_g$ from 0.75 to 0.97. However, only 3 mM (440 ppm) adipic acid is required to get most of that effect. As a result, organic acid additives will be less effective with low-sulfur coal, but much less additive will be required to get the maximum effect.

## BUFFER ALTERNATIVES

The model of gas/liquid mass transfer has also been used to give a quantitative comparison of buffer alternatives. Table 3 gives the buffer concentrations that would be equivalent in effectiveness to 11.8 mM adipic acid. Relative costs were calculated assuming that makeup is proportional to concentration.

Adipic acid is effective, nonvolatile, and has been extensively tested up to commercial-scale.

Dibasic acid (DBA) is a waste from adipic acid or caprolactam production containing primarily succinic, glutaric, and adipic acids. It is equivalent in effectiveness to adipic acid. DBA from Du Pont and Monsanto has been successfully tested at the pilot and commercial scale, but waste acids from Badische have produced some foaming problems in pilot plant testing (Chang and Dempsey, 1982). DBA is typically half the cost of adipic acid.

Formic and acetic acids are probably volatile under scrubber conditions. However, they may be used in a two-stage scrubber system with attention paid to recovery of the volatile acids.

Hydroxypropionic and hydroxyacetic (glycolic) acids are oxidation inhibitors and may also be less subject to oxidative degradation. Sulfosuccinic and sulfopropionic acids should give nonvolatile degradation products. Hydroxypropionic, sulfopropionic, and sulfosuccinic acids are not commercially available, but can be easily synthesized by addition of water or sulfite to acrylic acid or maleic anhydride. Hydroxyacetic acid is commercially available. It has a lower $pK_a$ value (3.85) than the other alternatives and should be relatively more effective in systems at lower pH.

## $SO_2$ REMOVAL/LIMESTONE UTILIZATION

Figure 2 shows that in actual scrubber systems the effect of adipic acid or DBA on $SO_2$ removal is evident at concentrations as low as 5 meq/L and asymptotes to gas-phase control at concentrations above 50 meq/L with 2800 ppm $SO_2$ (Mobley and Chang, 1981). These data also show that a number of sources of DBA give results identical to adipic acid when concentrations are expressed as meq/L.

Figure 3 demonstrates the typical effect of buffer additives on the

TABLE 3: RELATIVE COSTS OF ORGANIC ACIDS
(Rochelle et al, 1982a)

Ø=20, 55°C, pH 5.0, 0.1 M $CaCl_2$, 10 mM total sulfite, 1000 ppm$SO_{2i}$

| Organic Acid | Concentration (mM) | Price ($/lb mol) | Relative Cost |
|---|---|---|---|
| Formic | 21.1 | 12.28 | 0.28 |
| Acetic | 15.6 | 21.62 | 0.37 |
| Hydroxypropionic | 19.7 | 34.59[a] | 0.75 |
| Sulfosuccinic | 16.3 | 43.15[b] | 0.77 |
| Sulfopropionic | 25.6 | 34.59[a] | 0.97 |
| Adipic | 11.8 | 77.45 | 1.00 |
| Phthalic | 18.1 | 55.58 | 1.10 |
| Benzoic | 17.0 | 57.46 | 1.13 |
| Fumaric | 19.1 | 66.16 | 1.38 |
| Hydroxyacetic | 32.0 | 39.66 | 1.39 |
| Succinic | 12.3 | 134.11 | 1.80 |
| Lactic | 34.4 | 78.82 | 2.97 |

a Priced as acrylic acid.
b Priced as maleic anhydride.

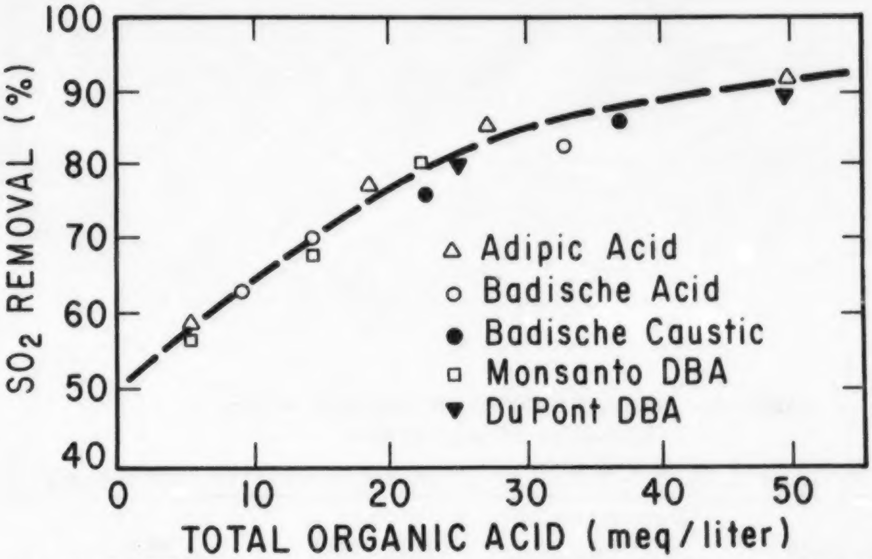


Figure 2. Measured effect of organic acids on SO$_2$ removal at the IERL-RTP pilot plant, pH 5.0, L/G = 9 l/m$^3$ (Chang and Mobley, 1982).

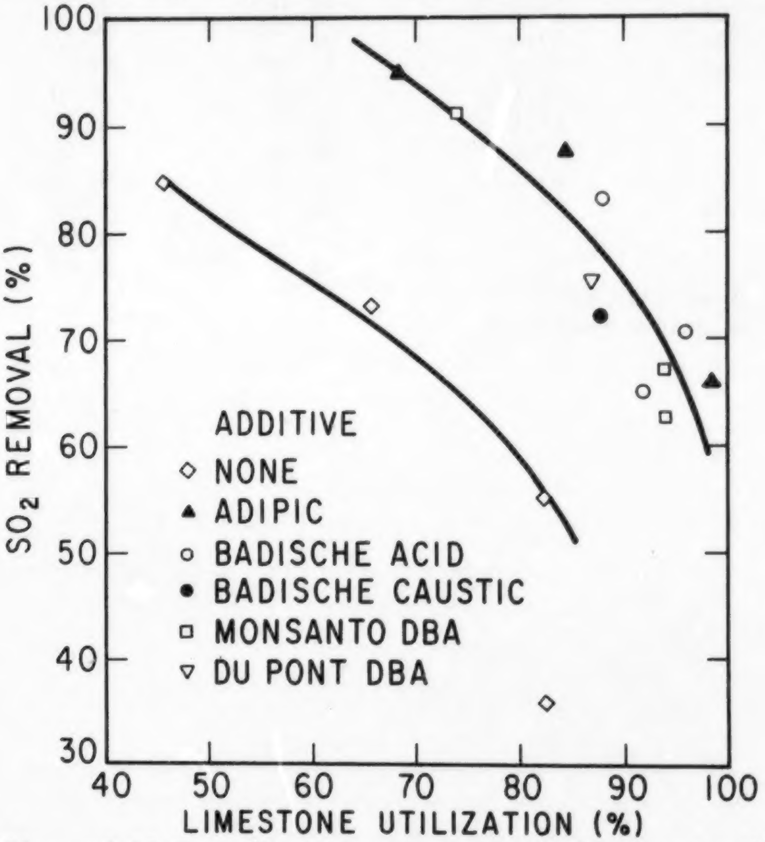


Figure 3. Effect of 13.7 meq/L of organic acids on limestone utilization and SO$_2$ removal, IERL-RTP pilot plant, L/G = 9 l/m$^3$, (Chang et al, 1982).

relationship of $SO_2$ removal to limestone utilization. The entire performance curve is shifted upward by the buffer additive so that the net effect can be improved $SO_2$ removal and/or limestone utilization. At constant $SO_2$ removal there is a tradeoff of limestone utilization (scrubber pH) and buffer concentration. Less buffer is required at low limestone utilization (high pH) than at high limestone utilization (low pH).

## L/G TRADEOFFS

The effect of buffer additives on scrubber performance is also apparent in the tradeoff of L/G and scrubber inlet pH (directly related to limestone utilization). Figures 4 and 5 give calculated results from the correlation of factorial data on the Shawnee spray tower (Burbank and Wang, 1982). The correlations are given as

Without forced oxidation:

$$\text{Fraction } SO_2 \text{ Removal} = 1 - \exp\left[-2.9\times10^{-4}(L/G)^{0.73}\exp\left(0.95\text{pH} + 4\times10^{-4}A\right)\right]$$

With forced oxidation:

$$\text{Fraction } SO_2 \text{ Removal} = 1 - \exp\left[-4.3\times10^{-3}(L/G)^{0.87}\exp\left(0.37\text{pH} + 4\times10^{-4}A\right)\right]$$

A is the concentration of adipic acid in ppm. These correlations were made with data over the ranges:

L/G = 54-150 gal/mcf

pH = 4.5-5.9

A = 0-2300 ppm

Gas flow rate = 20,000-35,000 acfm @300°F

Slurry flow rate = 1200-2400 gpm

Inlet $SO_2$ = 2360-3090 ppm

Figures 4 and 5 give L/G as a function of adipic acid concentration at 90% $SO_2$ removal. Typically 1500 ppm of adipic acid will reduce the required L/G a factor of 2.0. In general the effect of scrubber inlet pH on required L/G is less in the case of forced oxidation.

## OTHER EFFECTS

Few data are available on the interactions of buffer additives with the selection of limestone type and grind. One manifestation of improved scrubber performance can be equivalent $SO_2$ removal and limestone utilization even with a coarser limestone. Therefore, buffer additives will be more attractive in a system which is locked into a coarse limestone.

Buffer additives are effective even in the presence of high concentrations of $CaCl_2$. In recent tests at 50,000 ppm chloride (Chang and Laslo, 1982), 8.5 meq/l of DBA enhanced $SO_2$ removal from 55% to 80%. Mg additives

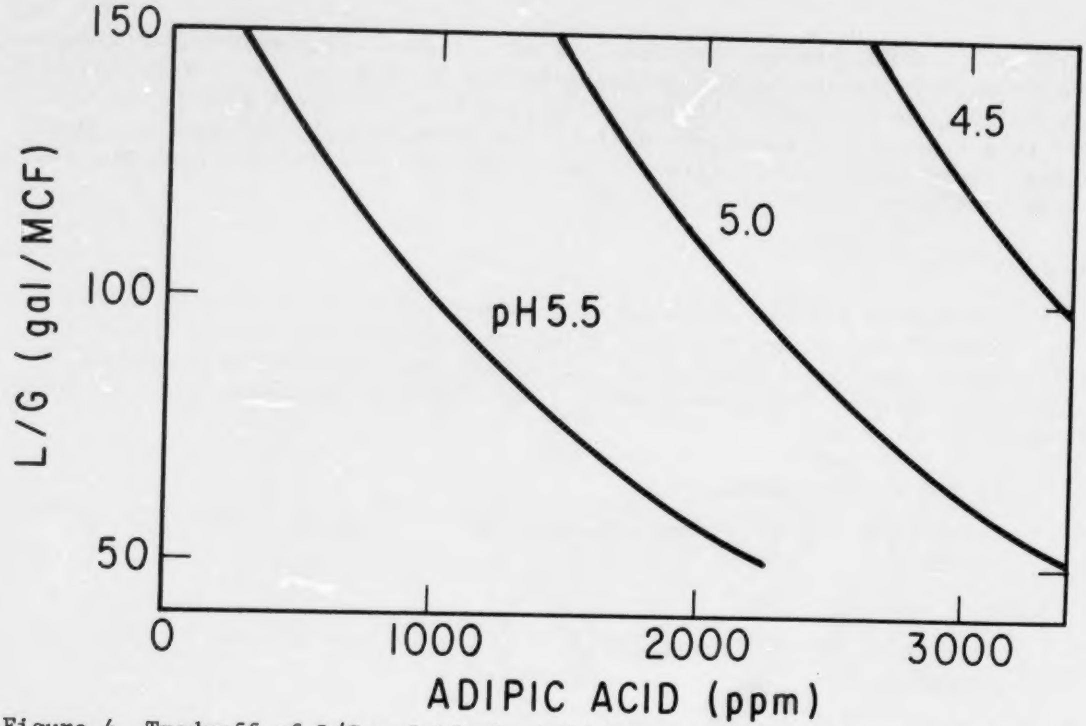


Figure 4. Tradeoff of L/G and Adipic Acid Concentration, Natural Oxidation, 90% $SO_2$ Removal, 2500 ppm $SO_2$, Spray Tower (Shawnee Correlation).

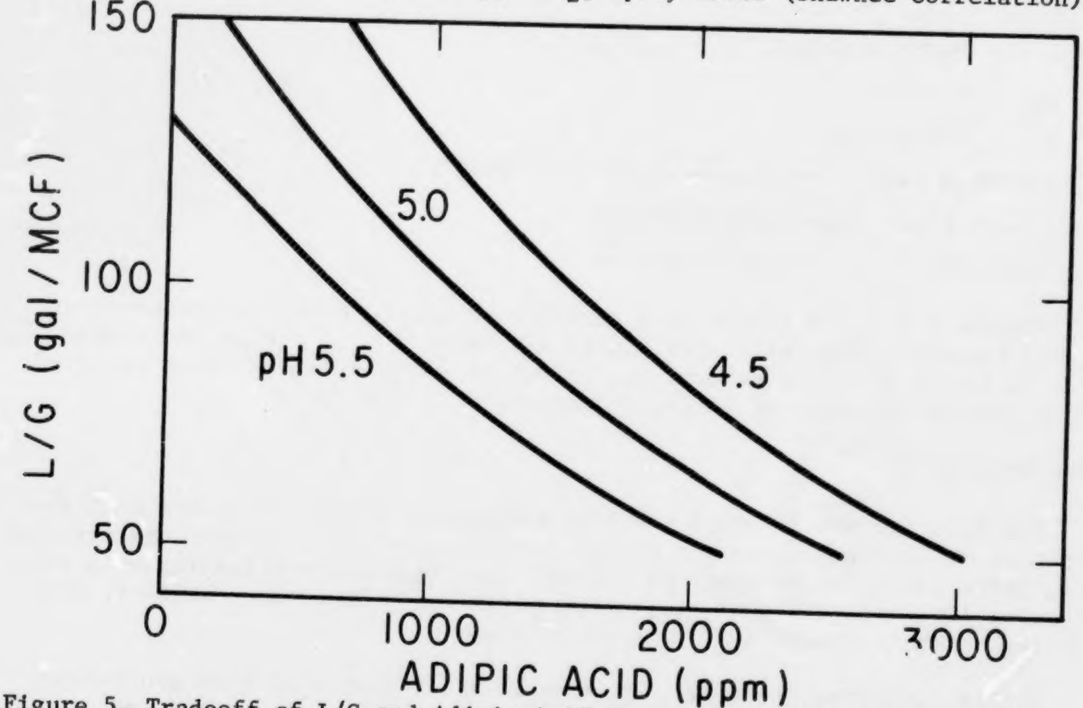


Figure 5. Tradeoff of L/G and Adipic Acid Concentration, Forced Oxidation, 90% $SO_2$ Removal, 2500 ppm $SO_2$, Spray Tower (Shawnee Correlation).

would be adversely affected by high chloride because the dissolved $Ca^{++}$ must be replaced by $Mg^{++}$ before significant enhancement occurs. Mg additives can also be adversely affected by forced oxidation in the scrubber loop, which has little effect on buffer additives.

## LOSSES OF ADDITIVE

Ideally, a buffer additive is retained in the scrubber solution and no makeup is required. Practically there are three important losses of soluble buffers:

1) Buffer is lost in the solution entrained with waste solids.

2) Organic acids degrade by conjugated oxidation with sulfite.

3) Buffer precipitates as pure solid or coprecipitates with $CaSO_3/CaSO_4$ solids and is lost in the waste solids.

Loss by volatilization is important for monocarboxylic acids such as formic, acetic, and benzoic, but should not be a problem with acids containing two hydrophilic groups, such as adipic or hydroxyacetic.

### LOSS AS ENTRAINED SOLUTION

The amount of additive lost as entrained solution varies directly with its concentration in the solution, the weight fraction solution in the waste solids, and the mass of the waste solids. Losses by this mechanism will be more significant without forced oxidation, without solids filtration or centrifugation, and with flyash removal in the scrubber loop.

### OXIDATIVE DEGRADATION

Adipic acid and other organic acids are usually stable to oxidation in aqueous solution. However, sulfite oxidation in the scrubber loop generates free radicals that attack carboxylic acids. Studies of this conjugated oxidation have shown that the rate of adipic acid degradation is directly proportional to the rate of sulfite oxidation and the adipic acid concentration (Rochelle et al, 1982a; Terry et al, 1982):

$$\frac{d[Ad]_T}{dt} = K_d \, [Ad]_T \, \frac{d[SO_3^{=}]_T}{dt}$$

Therefore oxidative degradation is potentially more important in systems with forced oxidation.

Figure 6 gives the measured values of the degradation rate constant as a function of pH and manganese ($Mn^{+2}$) concentration. The UT data were collected by batch oxidation of $CaSO_3$ slurry (Hsiang, 1981; Rochelle et al, 1982a, 1982b). The Radian data were collected in a bench-scale scrubber (Jarvis et al, 1982). The Shawnee data represent testing in 10 MW prototype scrubbers using limestone that typically generates 0.1 to 1.0 mM Mn (5 to 50 ppm) in solution. However solution analyses at Shawnee give total

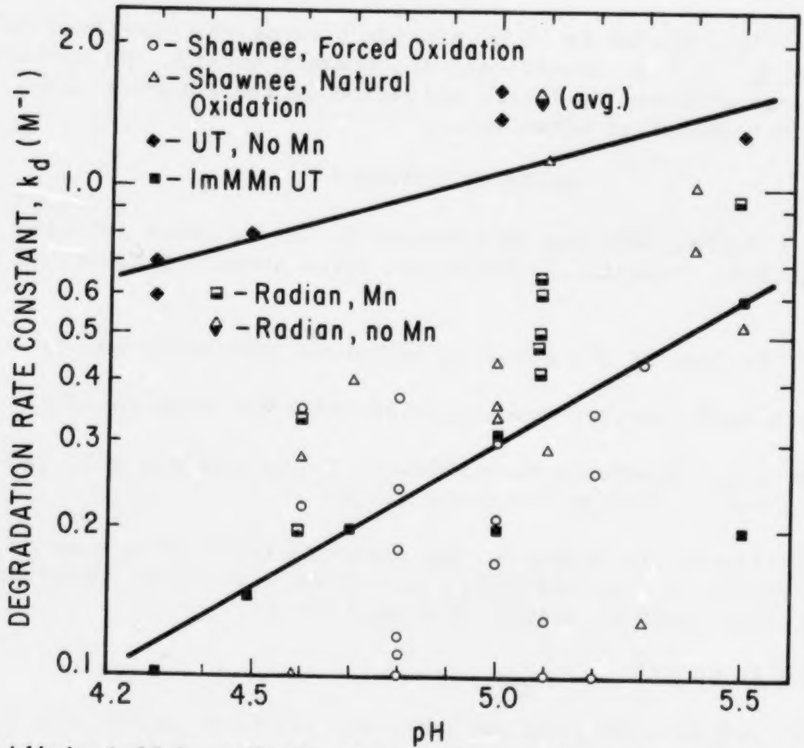


Figure 6. Adipic Acid Degradation Rates from UT (Rochelle et al, 1982b), Radian (Jarvis et al, 1982) and Shawnee (Burbank and Wang, 1981), Top Line without Mn, Bottom Line with Mn, 1.0 mM.

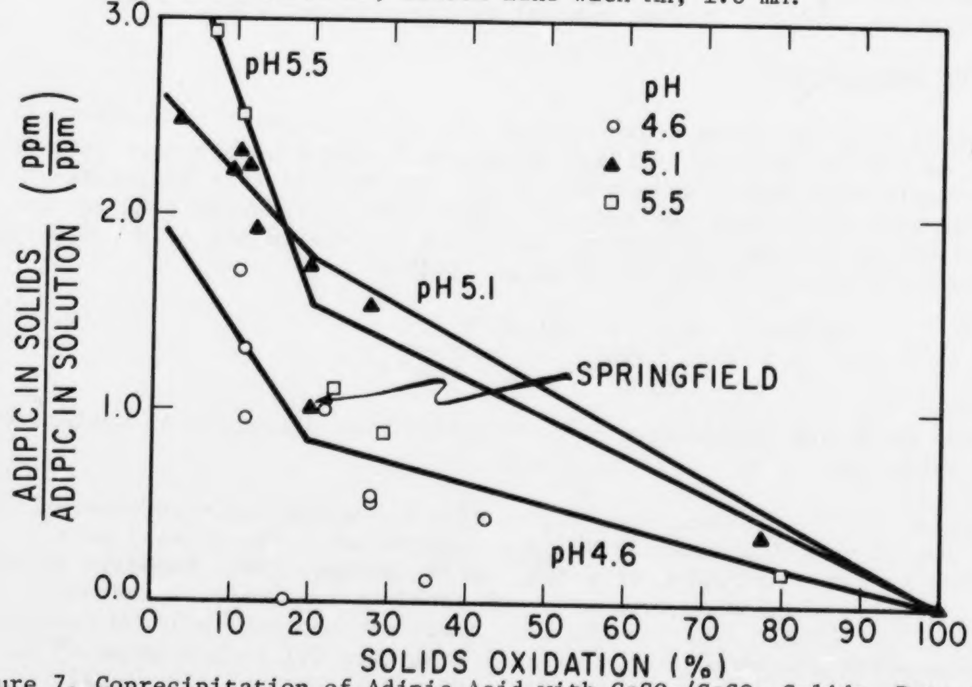


Figure 7. Coprecipitation of Adipic Acid with $CaSO_3/CaSO_4$ Solids, Data from a Bench-Scale Scrubber (Jarvis et al, 1982).

carboxylic acid, not adipic acid, so the calculated values of $K_d$ may be somewhat lower than the actual values.

In the presence of more than 0.1 mM Mn, the degradation rate decreases with decreasing pH and is substantially lower than in the absence of Mn. At pH 5.0 the degradation rate constant is about $0.3M^{-1}$ with 1 mM $Mn^{+2}$ and 1-2 $M^{-1}$ without $Mn^{+2}$.

Mn is probably derived as an impurity of limestone. In systems without forced oxidation it rarely gets above 0.1 to 0.2 mM and is typically less than 0.1 mM (Burbank and Wang, 1982). With forced oxidation in the scrubber loop it is typically greater than 0.2 mM and has been observed as high as 2.0 mM (Burbank and Wang, 1982). Therefore even though forced oxidation gives a greater rate of sulfite oxidation, it also increases the Mn concentration, so that the overall rate of degradation is not much worse than with natural oxidation.

The important degradation products of adipic acid result from successive decarboxylation. The gaseous products - $CO_2$, ethane, propane, and butane - represent loss of useable buffer. The products in solution - glutaric (pentanedioic), succinic (butanedioic), and valeric (pentanoic) acids and 4-carboxy-butanal (5-aldo-pentanoic acid) - are useful buffers and represent only partial loss of adipic acid. In one run without Mn, Radian (Jarvis et al, 1982) found that the moles of volatile hydrocarbon were equivalent to 57% of the moles of adipic acid lost (ethane - 12%, propane - 32%, butane - 13%). In nine runs with Mn, Radian (Jarvis et al, 1982) found that on the average 40% of the adipic acid lost could be accounted for as glutaric (28%), succinic (6%), and valeric (6%) acids. In the absence of Mn, there is less production of glutaric and succinic acids (Jarvis et al, 1982; Rochelle et al, 1982b). With low Mn the degradation products in solution include one unknown volatile acid and a nonvolatile acid tentatively identified as 4-carboxy-butanal. These solution products and smaller quantities of glutaric and succinic acids account for about 50% of the adipic acid degraded (Rochelle et al, 1982b).

Longterm operation of "closed" loop scrubber systems with buffer additives may result in the accumulation of degradation products. Run 917-1A on the Shawnee spray tower with scrubber-loop forced oxidation lasted for 70 days (Burbank and Wang, 1982). The analyzed concentration of total carboxylic acid was maintained at 18.5 meq/L for the first half of the run, then increased to 23.8 meq/L to maintain $SO_2$ removal. Later analysis of solution samples (Jarvis et al, 1982) at the end of the run gave 16.4 meq/L carboxylic acid (Shawnee silicic acid method) 10.8 meq/L buffer between pH 3 and 6 (Radian titration method), and only 7.0 meq/L adipic acid (ICE). Analyses by ion exclusion chromatography (ICE) and ion chromatography (IC) gave low concentrations of identifiable degradation products, but revealed an unknown (not yet identified) product equivalent to 6 meq/L (ICE) and 28 meq/L (IC) of adipic acid. The unknown product caused no operating problems but did affect the interpretation of Shawnee's analytical results. It behaves as a divalent acid with $pK_a$ values less than 3.0.

Degradation studies of buffers other than adipic acid have been conducted with batch oxidation of $CaSO_3$ slurry (Rochelle et al, 1982a,b). Malonic, succinic and glutaric acids degrade at essentially the same rates as adipic and give analogous products. Hydroxyacetic (glycolic) and hydroxypropionic acids are sulfite oxidation inhibitors. At 10 mM, these hydroxyacids inhibited oxidation completely at pH 4.5-5.0 in the absence of Mn. With 1 mM Mn, sulfite oxidation proceeded as usual, but there was no measurable degradation of the acids ($K_d < 0.1 M^{-1}$). In the absence of Mn at pH 4.5 with 2 mM hydroxyacid, there was typical sulfite oxidation and measurable, but low, degradation ($K_d = 0.2\text{-}0.4\ M^{-1}$). Lower degradation of adipic acid ($K_d = 0.15\ M^{-1}$) was also observed in the presence of 1 mM $MnSO_4$ and 10 mM hydroxyacetic acid at pH 5.5. It appears that free radical scavengers in the presence of Mn can serve to inhibit buffer degradation without completely stopping sulfite oxidation.

## LOSS AS SOLID

Ideally we do not expect buffer additives to precipitate with the waste solids, but rather to be retained in the scrubber solution. The solubility of calcium adipate is 0.11 M at 55°C (Hatfield and Potts, 1972), so it should not precipitate as pure solid at normal concentrations of 0.01-0.02 M total adipic acid. However analyses of $CaSO_3$ solids from the Radian bench-scale scrubber have shown that adipic acid precipitates as a solid solution with calcium sulfite hemihydrate.

Figure 7 shows that the ratio of adipic acid in the $CaSO_3/CaSO_4$ solids to adipic acid in solution varies with percent oxidation of the solids and pH of the solution. At 100% oxidation the gypsum solids typically contain less than 10 wt% of the adipic acid in the solution. However, at pH 5.5 and less than 10% oxidation, there was 3.0 times as much adipic acid in the $CaSO_3 \cdot 1/2\ H_2O$ solids as in the solution. In the range of 5 to 20% oxidation, the solids concentration of adipic acid varies with oxidation, perhaps because calcium adipate must compete with $CaSO_4$ for space in the $CaSO_3$ solid solution. Above 20% oxidation the sulfate content of the solid solution should not vary, so adipic acid content of the solids should decrease because there is a decreasing fraction of $CaSO_3$ solids.

Coprecipitation of the adipic acid appears to be more severe at pH 5.5 than at pH 4.6. The driving force for adipic precipitation is probably the concentration of calcium adipate which will be greater at higher pH and at higher dissolved calcium.

Limited results on coprecipitation from the Springfield demonstration are given on Figure 7 and confirm the benchscale tests. Coprecipitation was not generally significant in the Shawnee tests because oxidation was usually greater than 25%.

No data are available on coprecipitation of other buffers. Testing of DBA (mostly glutaric acid) in the 300 cfm pilot scrubber showed that its losses to degradation and coprecipitation at 15% oxidation were no more than 20% greater than the losses of adipic acid (Chang and Dempsey, 1982). The tendency of other buffers to coprecipitate is probably related to the solubility of their calcium salts.

## OVERALL EFFECTS

Table 4 summarizes adipic acid losses and makeup requirements for four hypothetical cases of systems using 10 mM (1460 ppm) adipic acid. In general the absolute makeup requirements will be directly proportional to the adipic acid concentration and to the amount of $SO_2$ removed. Applications with lower $SO_2$ gas concentrations will require lower adipic acid concentrations and remove fewer moles of $SO_2$, so the absolute makeup requirements will be much lower.

Case 1 shows that degradation losses dominate in systems with forced oxidation. Case 2 shows that solution and degradation losses are equally important in typical systems with natural oxidation. Total makeup requirements are about the same in systems with natural oxidation and systems with forced oxidation. Cases 3 and 4 demonstrate that inclusion of flyash in the waste solids or reduced dewatering greatly increases solution in losses and overall losses. Buffer additives will not be very attractive in systems without clarifiers and filters or centrifuges.

Table 5 demonstrates the tradeoff of pH with adipic acid makeup and limestone utilization at constant $SO_2$ removal. Lower pH appears to be better in systems with forced oxidation. Although a higher adipic acid concentration is required at lower pH, its degradation rate and total makeup requirement is lower. Furthermore, limestone utilization is better at low pH.

With natural oxidation, $SO_2$ removal is more sensitive to pH, so much less adipic acid concentration is required at high pH. At high pH sulfite oxidation is less but the degradation rate constant is larger. Nevertheless, the primary adipic acid losses at high pH result from coprecipitation and solution losses. With natural oxidation the optimum pH is a toss-up since reduced pH requires somewhat more adipic acid makeup but gives somewhat better limestone utilization.

Forced oxidation is especially attractive when used with adipic acid. It essentially eliminates solution and precipitation losses. It permits low pH operation with satisfactory $SO_2$ removal, which in turn gives nearly complete limestone utilization (even with a coarse grind). The combination of low pH and high Mn concentration minimizes buffer degradation.

## ENVIRONMENTAL IMPACT AND TOXICITY ASSESSMENT

Extensive tests on slurry and sludge from pilot and prototype scrubber tests of adipic acid and dibasic acid have shown that the additives introduce no additional problems of sludge toxicity or mutagenicity. Leached toxic elements were all present at levels below those deemed hazardous (Chang and Mobley, 1981; Epler et al, 1979). Biological tests including the Ames mutagenicity assay and CHO clonal toxicity assay have shown no mutagenicity and low or no detectable toxicity (Litton Bionetics, 1979, 1981, 1982).

Organic acid degradation will result in minor additional emissions of hydrocarbons (ethane, propane, butane) and volatile organic acids (valeric, butyric) in the flue gas and oxidizer vent. Chemical analysis of flue gas

### TABLE 4: ADIPIC ACID LOSSES WITH 10 mM (1420 ppm)
Calculated for Example Cases From Material Balance, Figure 6, and Figure 7

| Case | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Oxidation | 100 | 30 | 15 | 15 |
| wt % waste solids | 85 | 50 | 40 | 15 |
| wt % flyash in dry solids | 0 | 0 | 50 | 50 |
| $CaCO_3$ utilization | 90 | 80 | 70 | 70 |
| pH | 5.0 | 5.3 | 5.5 | 5.5 |
| Mn(mM) | 1.0 | 0.1 | 0.1 | 0.1 |
| Soln. losses gmol/gmol $SO_2$ | 0.32 | 1.61 | 5.22 | 19.7 |
| Degradation | | | | |
| $K_d(M^{-1})$ | 0.2 | 0.4 | 1.0 | 1.0 |
| mmol/gmol $SO_2$ | 2.00 | 1.20 | 1.50 | 1.50 |
| Coprecipitation | | | | |
| ppm solid/ppm solution | 0.07 | 0.35 | 1.25 | 1.25 |
| mmol/gmol $SO_2$ | 0.10 | 0.48 | 1.64 | 1.64 |
| Total Makeup Requirements | | | | |
| mmol/gmol $SO_2$ | 2.42 | 3.29 | 8.36 | 22.8 |
| lbs/ton $CaCO_3$ | 7.07 | 9.61 | 17.1 | 46.7 |

### TABLE 5: TRADEOFF OF ADIPIC ACID LOSSES AND pH
Basis: 90% $SO_2$ Removal, 3000 ppm Inlet $SO_2$, Spray Tower L/G = 100 gal/MCF, no flyash in solids; losses calculated from material balance, Figure 6 and Figure 7; adipic acid concentration calculated from Shawnee Correlation.

| pH | 4.5 | | 5.0 | | 5.5 | |
|---|---|---|---|---|---|---|
| $CaCO_3$ Utilization (%) | 99 | | 95 | | 80 | |
| $K_d(M^{-1})$ | 0.15 | | 0.30 | | 0.60 | |
| Oxidation | 50 | 100 | 35 | 100 | 15 | 100 |
| Adipic Acid (mM) | 23.0 | 10.5 | 14.9 | 7.3 | 6.7 | 4.1 |
| % Solids | 60 | 85 | 55 | 85 | 50 | 85 |
| Adipic Acid Losses (mmol/gmol $SO_2$) | | | | | | |
| Solution | 2.28 | 0.32 | 1.79 | 0.23 | 1.19 | 0.14 |
| Degradation | 1.74 | 1.58 | 1.57 | 2.19 | 0.60 | 2.46 |
| Coprecipitation | 0.89 | 0.02 | 2.32 | 0.05 | 1.95 | 0.10 |
| Total | 4.90 | 1.92 | 5.66 | 2.47 | 3.75 | 2.70 |

from the Shawnee venturi/spray tower gave about 2 $mg/m^3$ more polar organics (probably valeric acid) with adipic acid than from the TCA without adipic acid (Barbour et al, 1980).

Valeric and butyric acids from adipic or glutaric acid degradation have a low odor threshold. The odor has been occasionally observed in scrubber tests of adipic acid, but has never required remedial action or avoidance. The odor may be detectable over open tanks, but does not constitute a significant environmental impact.

## RELIABILITY/FLEXIBILITY

Buffer additives enhance scrubber reliability and operability by adding a degree of freedom to system operation and design.

Without additives, $CaSO_3$ scaling and plugged mist eliminators can result from the use of excess limestone, which may be necessary to get adequate $SO_2$ removal. Use of a buffer additive can permit satisfactory $SO_2$ removal at lower pH without excess limestone, thereby avoiding $CaSO_3$ precipitation in the scrubber and mist eliminator.

Use of buffer additives can permit simplification of scrubber internals to improve reliability while maintaining adequate $SO_2$ removal. Packing or trays that are easily plugged or TCA balls that collapse can be removed permanently from the scrubber system.

Control of $SO_2$ removal in response to system disturbances is easily achieved with buffer additives. Because of operation at lower pH, the scrubber pH responds more quickly to changes in limestone feedrate. Furthermore, $SO_2$ removal is typically less sensitive to changes in inlet $SO_2$ and gas flow rate. High levels of $SO_2$ removal (90 to 95%) are especially easy to control.

Buffer concentration can be adjusted to compensate for disturbances such as higher $SO_2$ concentration, higher gas flowrate, pump outages, and offspec limestone. If adequate feed system capacity is included, it is easy to increase the adipic acid concentration in the scrubber loop. However, reducing scrubber loop concentration can take a long time because of typically large clarifier inventories of buffer solution.

Limestone blinding by high $CaSO_3$ saturation was observed in tests of forced oxidation with adipic acid at both Shawnee and Springfield. Complete oxidation of both solid and dissolved sulfite was necessary to avoid $CaSO_3$ scaling and poor limestone utilization even at pH 4.6 to 5.0. Such blinding was also observed in tests without adipic acid. It is unclear whether or not blinding is a more severe problem in the presence of adipic acid.

## ECONOMICS

The cost of using adipic acid is primarily the operating cost of makeup. The capital cost of makeup facilities is small. The cost of initial inventory can be significant. Adipic acid costs about 60¢/lb. The makeup costs to maintain 10 mM can vary from \$4.20 to \$28.00/ton $CaCO_3$, depending on the conditions outlined in Table 4. DBA costs are typically about half of the adipic acid costs. Economically-optimum concentration levels of buffer additives may be substantially lower or higher than 10 mM.

The cost benefits of adipic acid also depend strongly on specific conditions, especially in existing scrubber systems. A switch from lime at \$60/ton to limestone at \$6/ton can save \$28/ton $CaCO_3$ in alkali makeup costs, though $CaCO_3$ grinding and adipic acid makeup facilities must be amortized. Buffer additives can permit the use of lower-cost higher-sulfur coal in existing scrubber facilities. Costly modifications in existing scrubber equipment can be avoided if buffer additives can be used to achieve $SO_2$ standards while maintaining reliable operation. Because of the minimal facilities required, buffer additives can be effectively used to buy time while more permanent fixes to system problems are being constructed.

Provision for the use of buffer additives in new facilities can result in reduced capital and operating costs for scrubber L/G and gas-side pressure drop and for limestone makeup and waste displosal. In one design comparison using forced oxidation with and without 1500 ppm adipic acid, Burnett et al (1982) showed that adipic acid makeup added only \$0.1/kw to capital costs and 0.15 mills/kwh to annualized operating costs, while it reduced total costs by \$20/kw and 1.77 mills/kwh, respectively.

Adipic acid reduces risk and increases flexibility in new designs. If the system is overdesigned, the user can reduce operating costs by using less or even no adipic acid. If the system is underdesigned, an increase in adipic acid makeup can be a timely, cost-effective fix. Increased flexibility also allows for system design based on average levels of $SO_2$ concentration and gas flow, rather than maximum levels.

## CONCLUSIONS

1. Adipic acid and waste dibasic acids have been demonstrated to enhance scrubber performance at concentration levels of 500 to 3000 ppm. At current conditions, the DBA additives are most attractive. Hydroxyacetic acid, sulfosuccinic acid, acetic acid, and other buffers should also be effective, but have not yet been adequately tested.

2. Buffer makeup costs are usually small compared to benefits. Solution losses must be minimized by solids dewatering. Degradation losses can be minimized by operating at lower pH in the presence of dissolved Mn. Losses by coprecipitation can be significant at higher pH in systems with less than 20% sulfite oxidation. Additional data are needed to quantify coprecipitation.

3. At constant $SO_2$ removal, overall losses of buffer are roughly independent of pH in systems with natural oxidation, but decrease with reduced pH in systems with forced oxidation.

4. Buffer additives will be relatively more useful in systems with solids dewatering, high sulfur coal, forced oxidation, and lower limestone

utilization.

5. In designs of new plants, substantial capital and operating cost savings can result from careful tradeoffs of $SO_2$ removal, buffer concentration, limestone utilization, and L/G.

6. In existing plants buffer additives can be used to increase $SO_2$ removal, switch from lime to limestone, avoid reliability problems, and reduce costs of power, maintenance, limestone makeup, and waste disposal.

7. There should be no significant additional environmental impact from the use of adipic or dibasic acids.

8. Future research and development work on buffer additives should include:

   a) Quantification of coprecipitation of $CaSO_3$ with adipic acid, DBA, and other buffer alternatives,

   b) Quantification and identification of buffer degradation products that can accumulate in longterm runs with closed-loop systems,

   c) Overall integrated system modeling to quantify design and operating tradeoffs,

   d) Testing of hydroxyacetic, sulfosuccinic, acetic, and other alternatives.

## NOMENCLATURE

$[Ad]_T$ - Total concentration of adipate and adipic acid, M

$[SO_3^{=}]_T$ - Total concentration of solid and liquid sulfite and bisulfite, M

$K_d$ - Organic acid degradation rate constant, $M^{-1}$

M - Molarity, gmol/liter

mM - Millimolarity, $10^{-3}$ gmol/liter

$pK_a$ - Buffer equilibrium constant

$K_g$ - Overall mass transfer coefficient based on $SO_2$ partial pressure, gmol/cm$^2$-atm

$k_g$ - Gas film mass transfer coefficient, gmol/cm$^2$-atm

$P_{SO_2}$ - Partial pressure of $SO_2$, atm

$\phi$ - Liquid film mass transfer enhancement factor

L/G - Scrubber liquid to gas ratio, gal/$10^3$ft$^3$

A - Adipic acid concentration, ppm

Mn - Manganese

## ACKNOWLEDGEMENTS

This review includes information obtained from a number of draft reports and progress reports of contracts supported by EPA/IERL. These sources include work by Radian, Acurex, and the University of Texas and were made available with the cooperation of David Mobley, John Chang, Jim Jarvis and others.

## REFERENCES

Barbour, R., et al, "Level 1 Assessment of Limestone Scrubbing with Adipic Acid Addition," EPA Contract No. 68-02-2686, Task 108, Battelle Columbus Laboratories (1980).

Borgwardt, R. H., "Significant EPA/IERL-RTP Pilot Plant Results," *Proceedings: Industry Briefing on EPA Lime/Limestone Wet Scrubbing Test Programs*, EPA-600/7-79-092, pp. 1-9, March 1979.

Behrens, G. P., and R. D. Delleney, "Evaluation of Adipic Acid Addition to a Bench-Scale Chiyoda Thoroughbred 121 FGD System," EPRI Report CS2185, December 1981.

Burbank, D. A., and S. C. Wang, "Test Reults on Adipic Acid-Enhanced Lime/Limestone Scrubbing at the EPA Shawnee Test Facility," presented at the Industry Briefing on EPA Lime/Limestone Wet Scrubbing Test Program, Raleigh, N.C., December 5, 1979.

Burbank, D. A., and S. C. Wang, "Test Results on Adipic Acid-Enhanced Limestone Scrubbing at the EPA Shawnee Test Facility - Third Report," *Proceedings: Symposium on Flue Gas Desulfurization* - *Houston*, *October*, *1980*, Vol. I, pp. 233-86, EPA-600/9-81-019a (1981).

Burbank, D. A., and S. C. Wang, "Adipic Acid-Enhanced Lime and Limestone Testing at the EPA Alkali Scrubbing Test Facility," EPA-600/7-82-010a, March, 1982.

Burnett, T. A., R. L. Torstrick, and F. A. Sudhoff, "Economic Evaluation of Alternative Limestone Scrubbing Options," presented at the EPA Symposium on Flue Gas Desulfurization, Hollywood, FL, May 1982.

Cavanaugh, C. M., "Buffer Additives for Flue Gas Desulfurization Processes," M.S. Thesis, University of Texas, Austin (1978).

Chan, P. K., and G. T. Rochelle, "Limestone Dissolution: Effects of pH, CO$_2$, and Buffers Modeled by Mass Transfer," *ACS Symp. Ser.*, in press, 1982.

Chang, C. S., and G. T. Rochelle, "Effect of Organic Acid Additives on SO$_2$ Absorption into CaO/CaCO$_3$ Slurries," *AIChE J.*, *28*, 261-66 (1982).

Chang, J.C.S., "Effect of Scrubbing Operating Conditions on Adipic Acid Degradation," Final Report, EPA Contract 68-02-3176, Task 4 (1980).

Chang, J.C.S., and J. H. Dempsey, "Pilot Plant Evaluation of Byproduct Dibasic Acids as Buffer Additives for Limestone Flue Gas Desulfurization Systems," EPA Symposium on Flue Gas Desulfurization, Hollywood, FL, May 1982.

Chang, J.C.S., and D. Laslo, "Chloride Ion Effect on Limestone FGD System Performance," presented at EPA Symposium on Flue Gas Desulfurization, Hollywood, FL, May 1982.

Chang, C. S., "Mass Transfer with Equilibrium Chemical Reaction, Sulfur Dioxide Absorption in Aqueous Solutions," Ph.D. Dissertation, University of Texas at Austin (1979).

Clarke, P. A., et al, "The Adipic Acid Enhanced Flue Gas Desulfurization Process for Industrial Boilers: Vol. I. Field Test Results," EPA/IERL-RTP 1335 (Draft), January 1982.

Colley, J. D., O. W. Hargrove, and J. D. Mobley, "Results of Industrial and Utility Boiler Full-Scale Demonstrations of Adipic Acid Addition to Limestone Scrubbers," presented at the EPA Symposium on Flue Gas Desulfurization, Hollywood, FL, May 1982.

Epler, J. L., et al, "Toxicity of Leachates," EPA-IAG-78-DX-0372, Oak Ridge National Laboratory, Oak Ridge, TN (1979).

Garcia, N. F., "Oxidative Degradation of Carboxylic Acids in the Presence of Sulfite," M.S. Thesis, University of Texas, Austin (1980).

Gerstle, R. W., D. S. Henzel, and J. D. Mobley, "Evaluation of the Adipic Acid Enhanced Limestone Flue Gas Desulfurization Process on an Industrial Boiler," presented at EPA's Industrial Briefing, Springfield, MO, July 15, 1981.

Hargrove, O. W., J. D. Colley, and J. D. Mobley, "Adipic Acid-Enhanced Limestone Flue Gas Desulfurization System Commercial Demonstration," presented at Coal Technology '81, Houston, TX, November, 1981.

Hargrove, O. W., et al, "Results of Full-Scale Adipic Acid FGD System Demonstration," draft report, EPA 68-02-3191, February 1982.

Hatfield, J. D., and J. M. Potts, "Removal of Sulfur Dioxide from Stack Gases by Scrubbing with Limestone Slurry: Use of Organic Acids," in Proceedings of Second International Lime/Limestone Wet-Scrubbing Symposium, APTD-1161, U.S. EPA, p. 263, 1972.

Hatfield, J. D., Y. K. Kim, and R. C. Mullins, "Study of the Effect of Organic Acids on the Wet Limestone Scrubbing Process," APTD 1137, PB 210-793, U.S. EPA, 1972.

Head, H. N., S. C. Wang, D. T. Rabb, R. H. Borgwardt, J. E. Williams, and M. A. Maxwell, "Recent Results from EPA's Lime/Limestone Scrubbing Program - Adipic Acid as a Scrubber Additive," Proceedings: Symposium on Flue Gas Desulfurization, Las Vegas, Nevada, EPA-600/7-70-167a, 343, (July, 1979).

Hicks, N. D., O. W. Hargrove, and J. D. Colley, "FGD Experiences - Southwest Unit I," Proceedings: Symposium on Flue Gas Desulfurization - Houston, October, 1980, EPA-600/9-81-019a, pp. 327-49 (1981).

Hicks, N. D., "Commercial Application Experience with Organic Acid Addition at Springfield City Utilities," presented at the EPA Symposium on Flue Gas Desulfurization, Hollywood, FL, May 1982.

Hollinden, G. A., N. D. Moore, and J. J. Schultz, "Removal of Sulfur Dioxide from Stack Gases by Scrubbing with Limestone Slurry: Effect of an Organic Additive at TVA Pilot Plant," presented at Fourth Annual Environmental Engineering and Science Conference, Louisville, KY, 1974.

Hsiang, M. W., "Degradation of Adipic Acid Conjugated with Sulfite Oxidation," M.S. Thesis, University of Texas, Austin, 1981.

Jarvis, J. B., J. C. Terry, S. A. Schubert, D. L. Utley, "Effect of Trace Metals and Sulfite Oxidation on Adipic Acid Degradation," EPA Contract 68-02-3171, Task No. 29, Draft Final Report, July 1981.

Litton Bionetics, Inc., "Level I Bioassays on Nine Conventional Limestone Scrubbing Samples with and without Adipic Acid Additive," EPA Contract No. 68-02-2681, Task 105, October 1979.

Litton Bionetics, Inc., "Cytotoxic Evaluation of L/S F.C. in the Rodent Cell (CHO) Clonal Toxicity Assay," LBI Project No. 22104 (October 1981).

Litton Bionetics, Inc., "Mutagenicity Evaluation of L/S F.C. in the EPA Level 1 Ames Salmonella/Microsome Plate Test," LBI Project No. 22104 (October 1981).

Litton Bionetics, Inc., "Cytotoxic Evaluation of Solid FGD Sludge Samples in the EPA Level 1 Roden Cell (CHO) Clonal Toxicity Assay," LBI Project No. 20993 (January 1982).

Litton Bionetics, Inc., "Mutagenicity Evaluation of Solid FGD Sludge Samples in the EPA Level 1 Ames Salmonella/Microsome Plate Test," LBI Project No. 20993 (January 1982).

Meserole, F. B., "Fate of Adipic Acid Used in FGD Systems," presented at ACS Southwest Regional Meeting, Austin, TX, December 5-7, 1979.

Meserole, F. B., D. L. Lewis, A. W. Nichols, and G. T. Rochelle, "Adipic Acid Degradation Mechanism in Aqueous FGD Systems," EPA-600/7-79-224, Semptember 1979.

Meserole, F. B., D. L. Lewis, and F. T. Kurzawa, "Further Study of Adipic Acid Degradation in FGD Systems," EPA-600/7-80-152, August 1980.

Mobley, J. D., and J.C.S. Chang, "The Adipic Acid Enhanced Limestone Flue Gas Desulfurization Process - An Assessment," JAPCA, 31, 1249-53 (1981).

Rochelle, G. T., "Process Synthesis and Innovation in Flue Gas Desulfurization," EPRI Report No. FP-463-SR (1977).

Rochelle, G. T., and C. J. King, "The Effect of Additives on Mass Transfer in $CaCO_3$ or CaO Slurry Scrubbing of $SO_2$ from Waste Gases," Ind. Eng. Chem. Fund., 16, 67 (1977).

Rochelle, G. T., and C. J. King, "Alternatives for Stack Gas Desulfurization by Throwaway Scrubbing," Chem. Eng. Prog., 65-70, February 1978.

Rochelle, G. T., Y. Lee, W. T. Weems, R. J. Smith, and M. W. Hsiang, "Buffer Additives for Stack Gas Desulfurization by CaO/$CaCO_3$ Slurry," draft final report (in preparation), EPA Grant R806743 (1982b).

Rochelle, G. T., W. T. Weems, R. J. Smith, and M. W. Hsiang, "Buffer Additives for Lime/Limestone Slurry Scrubbing," ACS Symp. Ser., in press (1982a).

Smith, R. J., "Synthesis of Organic Acids for Stack Gas Desulfurization by Aqueous Scrubbing," M.S. Thesis, University of Texas, Austin, 1981.

Terry, J. C., J. B. Jarvis, D. L. Utley, and E. E. Ellsworth, "Laboratory Investigation of Adipic Acid Degradation in FGD Scrubbers," presented at ACS National Meeting, Atlanta, GA, March 30-31, 1981.

Villiers-Fisher, J. F., and A. Warshaw, U.S. Patent 3,632,306 (1972).

Wang, S. C., and D. A. Burbank, "Adipic Acid-Enhanced Lime/Limestone Test Results at the EPA Alkali Scrubbing Test Facility," EPA Technology Transfer Capsule Report, EPA-625/2-82-029 (1981).

Wasag, T., J. Galka, and M. Fraczak, "Effect of Organic Acids on the Kinetics of $SO_2$ Absorption," *Air Conversation*, *9(3)*, 16 (1975).

Weems, W. T., "Enhanced Absorption of Sulfur Dioxide by Sulfite and Other Buffers," M.S. Thesis, The University of Texas, Austin (1981).

# RESULTS OF INDUSTRIAL AND UTILITY BOILER FULL-SCALE DEMONSTRATION OF ADIPIC ACID ADDITION TO LIMESTONE SCRUBBERS

by: J. D. Colley and O. W. Hargrove
Radian Corporation
Austin, TX 78766

J. David Mobley
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

## ABSTRACT

EPA's Industrial Environmental Research Laboratory at Research Triangle Park has conducted bench-, pilot-, and prototype-scale programs over the past several years to improve the performance of limestone flue gas desulfurization (FGD) systems. This paper describes the results of two demonstration-scale programs that were recently completed. Demonstration at a utility boiler FGD system was completed over a 9-month period (January-September 1981) at the Southwest Power Plant (SWPP) owned and operated by City Utilities of Springfield, MO. Natural and forced oxidation modes of operation were tested with both adipic acid and dibasic acid (DBA), a by-product of adipic acid manufacturing, used as buffers. The results of these programs show that the organic buffers substantially improve system performance. Also, the SWPP results could be predicted reasonably well from prototype-scale results which indicates that the prototype data base can be used effectively in the design of full-scale systems. Comparative economics for alternative methods of improving FGD system performance at SWPP indicate that DBA is the preferred choice for this system.

Demonstration at an industrial boiler FGD system was completed over a 1-month period (spring 1981) at the Rickenbacker Air National Guard Base. The $SO_2$ removal efficiency with the adipic acid averaged 94.3 percent over a 30-day period. In a prior test using only limestone, the system averaged 65.8 percent removal. Economic calculations for an industrial boiler adipic acid enhanced limestone FGD system indicate a slight reduction in both capital and operating expenses relative to a limestone-only system designed for 90 percent $SO_2$ control of 3.5 percent sulfur coal. The costs are competitive with the dual alkali system. The successful demonstration of the adipic acid enhanced limestone system increases the number of demonstrated technologies available to a potential user.

## INTRODUCTION

The majority of the flue gas desulfurization (FGD) systems in use today by the electric utility industry are lime or limestone based. Of these two, limestone systems are expected to predominate in the future because of economic reasons. However, designing limestone FGD systems for high $SO_2$ removal applications is particularly difficult due to the low reactivity (solubility) of this reagent. This requires higher liquid-to-gas (L/G) ratios and larger reaction tanks compared to other FGD processes. A number of systems have been marginally designed and, in many instances, actual $SO_2$ removal efficiencies are lower than that required by regulation.

As the result of these concerns, EPA's Industrial Environmental Research Laboratory at Research Triangle Park (IERL-RTP) embarked on extensive laboratory-, pilot-, and prototype-scale studies to enhance the performance of lime/limestone systems. Most of this effort has been focused on use of adipic acid as a buffering agent. The initial testing indicated that adipic acid enhanced limestone FGD systems offered the following improvements compared to unenhanced systems:

- Higher $SO_2$ removal.
- Increased limestone utilization.
- Projected lower capital and operating costs.
- Greater system flexibility.
- Lower cost sorbent promotes the use of limestone rather than more expensive and energy intensive lime.

In addition to these advantages, adipic acid offered the potential to improve the performance of many of the marginally designed existing systems. Based on the prototype results, the EPA conducted two full-scale demonstrations of the use of adipic acid in limestone based FGD systems. For the electric utility demonstration program, EPA contracted with Radian Corporation to perform the work at Southwest Power Plant (SWPP), owned and operated by City Utilities of Springfield, MO. EPA contracted with PEDCo Environmental, Inc. and Radian to conduct the industrial boiler demonstration at Rickenbacker Air National Guard Base (RANGB) near Columbus, OH. The utility-scale demonstration testing lasted a total of 9 months. The industrial-scale demonstration took place over a 30-day period. This paper presents a summary of the results of these two programs.

## UTILITY BOILER DEMONSTRATION

The primary objective of this program was to document the effectiveness of adipic acid as an enhancement agent in a limestone FGD system treating flue gas from a utility boiler burning a high sulfur coal. To demonstrate the flexibility of adipic acid, the test program included operation of the scrubbers in both the natural and forced oxidized configurations. Another important objective was to test the validity of the Shawnee data base, thereby demonstrating the usefulness of that information as a tool in designing full-scale FGD systems.

The testing was conducted with a continuous $SO_2$ monitoring system installed, certified, and operated according to EPA protocol. In addition to the adipic acid testing, 1 month of work with an alternate organic buffer (dibasic acid) was conducted to compare its performance to that of adipic acid. Near the end of the testing phase, an economic analysis to determine the most cost effective means of achieving compliance $SO_2$ removal efficiencies for the SWPP scrubbers was conducted. The cost comparisons of the three options chosen were based on information gathered over the course of the testing.

## SYSTEM DESCRIPTION

Springfield City Utilities' Southwest Unit 1 is a 194 MW coal-fired unit designed to burn 3.5 to 4.0 percent sulfur coal. After exiting the boiler, flue gas passes through the air preheater, electrostatic precipitator, and induced draft fans prior to entering the FGD system and subsequently exiting the plant through the stack.

The FGD system, as originally designed, consisted of two parallel turbulent contact absorber (TCA) scrubber modules, each sized to handle 60 percent of the design flue gas flow. One of these modules (S-1) was converted to a tray absorber in May 1981, and the other (S-2) was converted in October 1981. The conversion consisted of replacing each of the three levels of TCA sphere cages with stainless steel perforated trays. Limestone preparation and sludge handling systems are common to the two FGD modules.

Figure 1 shows the flow schematic for one of the two modules. The gas enters the presaturator and is cooled by supernatant liquor (thickener overflow). The gas then passes through three contactor levels (where gas/slurry contact and $SO_2$ removal are accomplished), the mist eliminator, and out the stack. The lower bank of mist eliminator blades is washed with supernatant liquor to minimize scaling and plugging problems.

Two relatively simple process modifications were made for the test program: an adipic acid feed system and a forced oxidation system were installed. Both systems were designed for temporary use during the test program and, as a result, did not offer all of the advantages of permanent installations. The adipic acid feed system consisted of a 2-ton (1.82 MT) vibrating silo, a screw conveyor, and a vibratory screw feeder. The adipic acid was fed to the limestone sump, mixed with freshly ground limestone, and then transferred to the limestone storage tank. Since the limestone preparation equipment was common to the scrubber modules, both scrubbers usually operated with about the same adipic acid concentration.

The forced oxidation system consisted of four 1800 scfm (50 $Nm^3$/min) compressors, air distribution valves and piping, and an air sparger for each module. Air flow to each sparger could be controlled independently so that oxidation air stoichiometry set points could be maintained. The spargers were located near the perimeter of the reaction tanks and about 2 ft (0.61 m) above the bottom. They consisted of 6-in. (15.2 cm) Schedule 40 pipe with 1-in. (2.5 cm) holes through which the air was introduced into the slurry. This design limited the shear stress exerted by the air on the agitator. However, the agitator horsepower was not used to help distribute the air as might be recommended in a permanent installation. The expense of upgrading the agitator assembly could not be justified for a 3-month program.

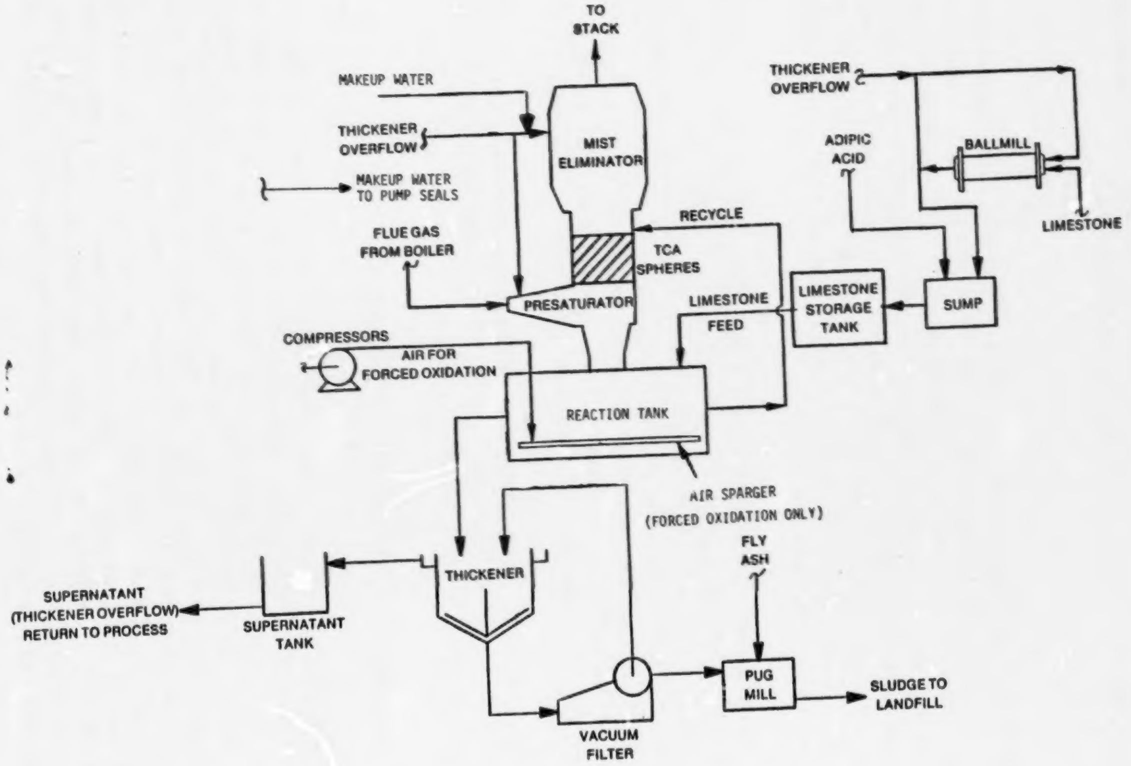


Figure 1. Southwest Unit 1 scrubber module flow diagram.

## FORCED OXIDATION TEST RESULTS

A summary of the results of the forced oxidation testing is presented in Table 1. Since City Utilities was planning to change the TCA modules to tray modules, some testing without the TCA spheres was conducted on one module. Also, complete oxidation of the sulfite in Module S-1 could not be achieved due to maintenance problems with the compressors.

### $SO_2$ Removal

Table 1 shows that addition of adipic acid to about 1300 ppm concentration improved the $SO_2$ removal from below 50 percent efficiency (baseline) to about 84 percent efficiency without the TCA spheres. The regulation in force at SWPP (1.2 lb $SO_2/10^6$ Btu (516 ng/J) emissions limit) typically requires between 82 and 85 percent $SO_2$ removal. Greater than 90 percent $SO_2$ removal was achieved with over 2000 ppm adipic acid and $5.6^+$ pH in a short-term test not shown in Table 1. However, long-term operability of the system under these conditions was not examined.

In 49 days of testing with TCA spheres in Module S-2, average process control settings of 2400 ppm adipic acid concentration and 5.0 pH resulted in 91 percent $SO_2$ removal (at baseline conditions, $SO_2$ removal averaged 58 percent). This included the start-up and optimization period when problems with limestone blinding and water balance closure were encountered and solved. During a 2-week period in April, the average $SO_2$ removal was 96 percent, and 95 percent daily average $SO_2$ removal was achieved on all but 2 days.

Comparison of $SO_2$ removal data from the full-scale demonstration to the prototype data shows fairly good agreement. A correlation was developed by Bechtel from the Shawnee prototype results (1):

$$\text{Fraction } SO_2 \text{ Removal} = 1 - \exp\{-0.0047 \exp(\text{pH} + 0.00062 \text{ Ad})\} \qquad (1)$$

where Ad and pH represent the adipic acid concentration in ppm and the pH of the scrubber feed liquor, respectively. The Shawnee correlation predicts $SO_2$ removals which are 2 to 5 percent higher on the average than the actual results observed at SWPP. Differences in Shawnee and SWPP scrubber operation include a slightly lower TCA sphere charge at SWPP and slightly lower slurry and gas flow rates (on an equivalent cross sectional area basis). Also significant maldistribution of TCA spheres noted at the end of the forced oxidation program at SWPP would contribute to this difference. The conclusion which can be drawn from this comparison is that the Shawnee data base can be used as an effective design tool. Good engineering practice should include exercising some conservatism, however.

The full-scale data at SWPP were correlated using the same form as in Equation (1):

$$\text{Fraction } SO_2 \text{ Removal} = 1 - \exp\{-0.00415 \exp(\text{pH} + 0.00065 \text{ Ad})\} \qquad (2)$$

TABLE 1. SUMMARY OF FORCED OXIDATION TESTING

| | Operating Time, days | Scrubber Feed pH | Adipic Acid ppm | Atoms O/ Mole $SO_2$ Removed | $SO_2$ Removal, % | Limestone Utilization, % | Sulfite Oxidation, % |
|---|---|---|---|---|---|---|---|
| Testing Without TCA Spheres (Module S-1) | | | | | | | |
| Baseline | 20 | 5.4 | 0 | 3.1 | 46 | 89 | 95 |
| Adipic Acid Addition | 6 | 5.4 | 1340 | 2.8 | 84 | 89 | 90 |
| Testing With TCA Spheres | | | | | | | |
| Baseline - Module S-2 | 24 | 5.4 | 0 | 3.0 | 58 | 88 | 91 |
| Adipic Acid Addition - Module S-2 | 49 | 5.0 | 2410 | 3.0 | 91 | 92 | 94 |
| Module S-1 | 40 | 5.1 | 2340 | 1.3 | 89 | 91 | 74 |

Figure 2 shows the predicted $SO_2$ removal using Equation (2) versus observed values. Although the data are scattered as might be expected in full-scale operation, 90 percent removal was routinely achieved with an adipic acid concentration of 2000 ppm and a scrubber feed pH of 5.

### Limestone Utilization

Table 1 shows that limestone utilization remained high throughout the forced oxidation testing. When periods of sulfite blinding of the limestone were discounted, the average limestone utilization was ∿90 percent with and without adipic acid. Note that the solid phase residence time in the reaction tank was almost halved when adipic acid was added (due to higher $SO_2$ removals) which could have contributed to relatively lower limestone utilization in the adipic acid testing. Without additional parametric testing, however, improvement in limestone utilization due to addition of adipic acid cannot be concluded from the data gathered in the demonstration program. Nevertheless, limestone utilization at constant $SO_2$ removal would be expected to be much greater with adipic acid addition than without it, due to the ability to operate at a lower pH with adipic acid.

## NATURAL OXIDATION TEST RESULTS

After a 1-month scheduled maintenance outage in May 1981, natural oxidation testing was conducted over the summer. The results of this testing are summarized in Table 2. One of the modules was converted to a tray tower in May, and the tray void area was reduced to increase the gas-side pressure drop after about 6 weeks into the natural oxidation testing.

### $SO_2$ Removal

Much of the testing in the natural oxidation mode centered around defining conditions to meet 85 percent $SO_2$ removal since City Utilities was interested in gaining experience operating the system under conditions required to meet their emissions' regulation. Table 2 shows that the 85 percent removal goal was achieved over a range of conditions. After the tray tower was modified to increase the pressure drop, 85 percent $SO_2$ removal was achieved at an average pH of 5.2 and 760 ppm adipic acid concentration at full load conditions. Removal of 85 percent was also achieved at 5.5 pH and 640 ppm adipic acid concentration at full load conditions. Note that these operating conditions resulted in daylong average $SO_2$ removal efficiencies of about 90 percent.

Table 2 also shows that the performance of the TCA module deteriorated over the course of the natural oxidation test program. Note that only 78 percent removal was achieved in the TCA compared to 91 percent removal for the tray tower in the third set of 85 percent removal tests. Plugging in the TCA cages was at least partially responsible and will be discussed in the section entitled "Operating Benefits/Difficulties."

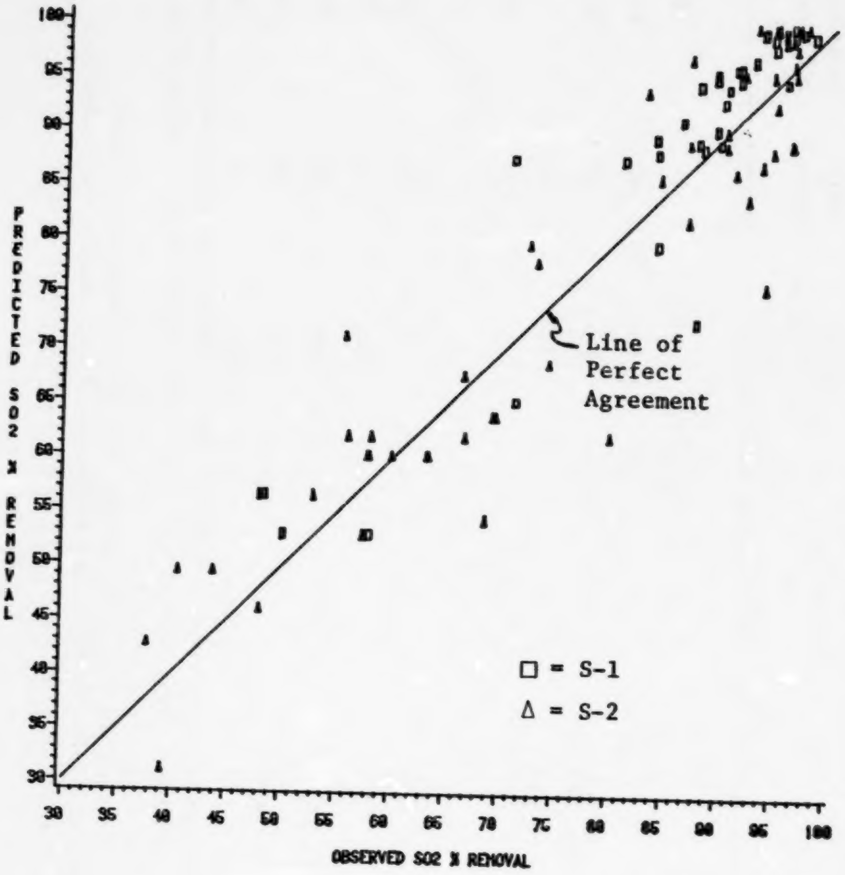


Figure 2. Fit of Springfield forced oxidation data to revised Bechtel model. Fraction $SO_2$ Removal = 1 - exp{-0.00415 exp(pH + 0.00065 Ad)}

TABLE 2. SUMMARY OF NATURAL OXIDATION TESTING

| | Operating Time days | pH | Adipic Acid Conc. ppm | $SO_2$ Removal % | Limestone Utilization % |
|---|---|---|---|---|---|
| Tray Tower | | | | | |
| Baseline* | 24 | 5.6 | 0 | 68 | 79 |
| Goal - 85% Removal* | 17 | 5.4 | 1000 | 87 | 81 |
| Goal - 85% Removal (5.2 pH) | 12 | 5.2 | 760 | 90 | 86 |
| Goal - 85% Removal (5.5 pH) | 10 | 5.5 | 640 | 91 | - |
| Goal - 95% Removal | 17 | 5.4 | 1750 | 96 | 78 |
| TCA Tower | | | | | |
| Baseline | 24 | 5.6 | 0 | 72 | 69 |
| Goal - 85% Removal | 17 | 5.3 | 890 | 91 | 92 |
| Goal - 85% Removal (5.2 pH) | 12 | 5.2 | 700 | 88 | 82 |
| Goal - 85% Removal**(5.5 pH) | 10 | 5.4 | 550 | 78 | 75 |
| Goal - 95% Removal** | 13 | 5.2 | 1690 | 94 | 86 |

*The void area in the tray tower was about 10 percent higher during these test periods than in the later test periods.

**These goals were obtained in the tray module but not in the TCA module. Deteriorating conditions in the TCA module and a common adipic acid addition system prevented the goals from being attained in the TCA module.

Since one module had been converted to a tray tower and the other suffered from reduced performance efficiency, there are difficulties comparing the full-scale results directly with the Shawnee prototype results. This is further complicated by the fact that most of the correlations reported for prototype natural oxidation testing have been derived from high pH runs (pH $5.6^{+}$). Spot checks of the full-scale data taken at higher pHs and early in the program when the TCA module was performing better indicate that the Shawnee correlations predict full-scale results reasonably well. As in the forced oxidation testing, the prototype correlation predicts slightly higher $SO_2$ removals than those actually achieved at full scale.

The data from the tray tower in the demonstration program were fit to the following equation:

$$\begin{matrix}\text{Fraction } SO_2 \\ \text{Removal}\end{matrix} = 1 - \exp\{-0.00131\ Ad - 0.00216\ \exp(pH) - 0.0996\ L/G\} \quad (3)$$

Figure 3 shows the agreement between the actual $SO_2$ removal and the removal predicted from Equation (3). This equation was developed to describe the trends noted during the program, and caution should be applied in using the equation since parametric testing was not performed during the demonstration. Note that the liquid and gas rates were clearly important variables in $SO_2$ removal during natural oxidation testing. Due to data scatter and the relatively small range of $SO_2$ removals resulting from the 95 percent removal goal, the effect of L/G was not observed in the forced oxidation test data.

## Limestone Utilization

Table 2 also summarizes the limestone utilizations measured in the natural oxidation testing. As in the forced oxidation phase, the averages from the natural oxidation phase do not show that the adipic acid system has a clear-cut advantage with respect to limestone utilization. There are several reasons why improvements in the utilization were not seen in the averages. First, compared to the baseline testing with no adipic acid in the system, the residence time of the solids in the reaction tanks was generally about 10 hours less during the adipic acid testing due to the higher $SO_2$ removal (and solids generation) rates. The decreased time available in the reaction tank for limestone dissolution requires higher limestone feed rates which results in lower limestone utilization. Secondly, $SO_2$ removal efficiencies during the baseline testing did not approach the efficiencies seen during testing with adipic acid. For the scrubbers to get equivalent removals without the addition of adipic acid would require operation in the pH range of 5.8 to 6.0 and also require improvements in gas/liquid contacting. The effect of pH on limestone utilization in a single loop system is well documented, with increases in pH accompanied by lower limestone utilizations. The numbers in Table 2 are averages over each period. Scrubber pHs were generally controlled in the 5.2 to 5.5 range. There were several days during baseline testing when the scrubbers were controlled at pH 5.8 and utilizations were measured as low as 55 percent. This verifies the effect of pH on utilization and also shows that improvements in utilizations were seen but were masked by the averages that were presented in Table 2.

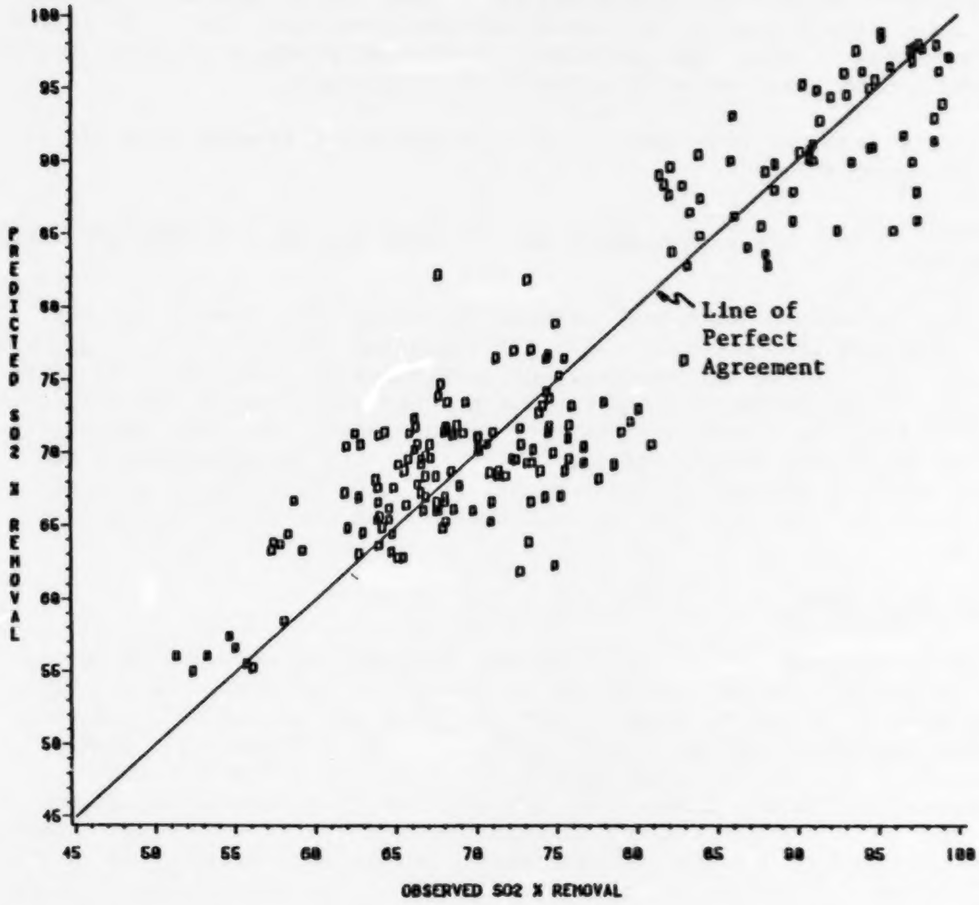


Figure 3. Fit of Springfield tray tower data to model. Fraction $SO_2$ Removal = 1 - exp{-0.00131 Ad - 0.00216 exp(pH) - 0.0996L/G}

## ADIPIC ACID CONSUMPTION

Table 3 summarizes the adipic acid material balances made for both the natural and forced oxidation phases of the program. The actual-to-theoretical ratio averaged 9 for the forced oxidation phase and about 5 for the natural oxidation phase. These are somewhat higher than those reported in the Shawnee prototype testing (2), but are roughly equivalent to values obtained in bench-scale testing under similar conditions (3). The actual-to-theoretical ratio for forced oxidation indicates that chemical degradation was higher in that test phase.

The adipic acid consumption in pounds per ton of $SO_2$ removed may be a useful ratio in estimating consumption for proposed systems. Note that for the TCA/tray combination, the adipic acid consumption triples when the $SO_2$ removal is increased from 85 to 95 percent (11 to 29 lb adipic acid/ton $SO_2$ (5.5 to 14.5 g/kg)). Also note that the consumption rates in the forced oxidation phase were lower than during natural oxidation testing (18 compared to 29 lb/ton $SO_2$ (9 versus 14.5 g/kg)) at 95 percent $SO_2$ removal. The lower losses in the filter cake due to higher solids content more than compensated for higher chemical degradation caused by increased sulfite oxidation.

## OPERATING BENEFITS/DIFFICULTIES

In addition to the obvious benefit of increased $SO_2$ removal, other operating improvements were noted during the demonstration program. The most obvious was the improved system reliability over the course of the test program (Table 4). Overall, the scrubbers operated for about 85 percent of the time (from March through August 1981) which is a great improvement over previously reported reliability. This improvement is a result of a number of mechanical changes implemented by the City Utilities staff, some revised process operating procedures, and additional process engineering input as well as to the addition of adipic acid.

During the forced oxidation program, almost 36 days of continuous operation were logged for both modules. At the end of the testing, there was little solids buildup either in the TCA cages or mist eliminators. In natural oxidation, the reliable operation continued, although there was some buildup of solids, particularly in the TCA cages. The mist eliminators also were plugged, but the major cause of this was probably due to plugged mist eliminator wash nozzles. The excellent performance during forced oxidation is due to the relatively high limestone utilization and large amount of gypsum seed crystals available for precipitation. In general, the pH set point was higher in the natural oxidation phase which resulted in lower limestone utilization. Additional calcium carbonate and calcium sulfite dissolution can increase the tendency to scale or plug. (Note that the tray module had little solids buildup on the trays, and the solids present were cleaned with a minimum of effort. This should improve scrubber module reliability in the future.)

## TABLE 3. ADIPIC ACID MATERIAL BALANCE RESULTS

| | Forced Oxidation* (95% Removal) | | Natural Oxidation 85% Removal | | Natural Oxidation 95% Removal | |
|---|---|---|---|---|---|---|
| Adipic Acid Addition, lb/hr (kg/hr) | 80 | (36) | 46 | (21) | 113 | (51) |
| Adipic Acid Losses in Sludge Liquor, lb/hr (kg/hr) | 13 | (6) | 10 | (5) | 21 | (10) |
| Actual/Theoretical Ratio** | 9 | | 4.8 | | 5.4 | |
| Adipic Acid Consumption, lb/ton $SO_2$ removed (g/kg) | 18 | (9.0) | 11 | (5.5) | 29 | (14.5) |
| Cost (¢/kWh)*** | 0.029 | | 0.017 | | 0.047 | |

*During forced oxidation, adipic acid was frequently lost in slurry discharged during upsets in dewatering plant operations. These numbers have been adjusted, based on the quantity of these losses, to reflect more normal operation.

**Actual/theoretical ratio = actual adipic acid added/adipic acid lost in sludge liquor.

***Cost of adipic acid assuming 60¢/lb ($1.32/kg).

TABLE 4. SCRUBBER RELIABILITY* DURING ADIPIC ACID DEMONSTRATION PROGRAM (1981)

| | Module S-1 | Module S-2 |
|---|---|---|
| January 10-31 | 66 | 85 |
| February | 54 | 35 |
| March | 88 | 81 |
| April | 67 | 97 |
| May | 87 | 66 |
| June | 78 | 74 |
| July | 94 | 94 |
| August | 90 | 80 |
| Average January 10 - August 31 | 79 | 86 |
| Average March 10 - August 31 | 86 | 87 |
| Average 1979 Scrubber Reliability | 34 | 42 |
| Average 1980 Scrubber Reliability | 59 | 31 |

*Defined as $\frac{\text{hours operated}}{\text{hours required}}$ x 100.

The conclusion drawn from the testing is that addition of adipic acid, while not the sole contributor to improved reliability at SWPP, can allow a system to operate with higher limestone utilization which should improve system performance. This was noted particularly in the forced oxidation testing at SWPP. Periods of fairly high pH and low limestone utilization in the natural oxidation phase resulted in less favorable performance than in the forced oxidation phase.

Although overall system performance was excellent during most of the program, problems with the air compressors, dewatering equipment, and adipic acid feed system caused operating difficulties which had to be overcome. A number of problems with the air compressors restricted their availability so that generally only two or three of the four compressors were in use at any time. When the system is not quite fully oxidized, concentration of dissolved sulfite increases, and the sulfite apparently precipitates on the surface of the limestone particles causing blinding. The result in forced oxidation was a rapid drop in pH and loss of $SO_2$ removal efficiency. This blinding seems to be a particular problem at 90 to 95 percent oxidation levels. Blinding can be solved quickly by increasing the oxidation air rate which appears to oxidize the sulfite layer off the limestone surface. Unfortunately, with low compressor availability, both modules could not be fully oxidized: one module averaged about 75 percent oxidation while the other averaged $99^+$ percent. Blinding in both modules was avoided for about the last 3 weeks of forced oxidation testing.

Some apparent blinding was also noted during natural oxidation, particularly during 95 percent $SO_2$ removal testing. The effect while operating in the natural oxidation mode was loss of pH control, although the pH did not drop off rapidly as in forced oxidation. The pH control was sluggish, and in some cases (with a pH 5.5 set point) the limestone feed could be turned either full on or off for 2 hours or longer with no noticeable change in pH. Obviously, this type of blinding can reduce limestone utilization.

Problems in dewatering were mainly associated with forced oxidation, although the problems with the dewatering system design remained to a lesser extent in natural oxidation testing. In forced oxidation, the gypsum settled quickly in the inner area of the thickener and plugged the underflow lines. The system could not handle the fully oxidized material and had problems even with the partially oxidized solids through most of the testing. Rapid settling and relatively low slurry velocities in the underflow lines caused many periods when these lines had to be flushed. The resulting losses of slurry laden with adipic acid occurred through much of the forced oxidation program. These types of problems could be alleviated with a dewatering system specifically designed to handle gypsum. Fugitive water losses were greatly reduced (although not eliminated) in natural oxidation testing.

The last major problem was caused by the temporary adipic acid feed system. First, although the sacks of adipic acid were reportedly weatherproof, the adipic acid apparently picked up moisture during summer months, causing troublesome lumps. In addition, the automatic feeder discharged directly into the open limestone sump. This area was extremely humid with steam rising from the 160°F (70°C) limestone slurry. As a result, the adipic acid feed system plugged frequently, particularly in the summer. Again, a properly designed adipic acid feed system should reduce the frequency with which plugging problems occur.

## DBA TESTING

One month of testing with an alternative organic buffer, dibasic acid (DBA), was completed in early October. DBA is a by-product of the manufacture of adipic acid and is significantly less expensive. It is a mixture of glutaric, adipic, and succinic acids with glutaric acid being the major species. Results of the testing are summarized in Table 5.

Table 5 shows that the tray tower achieved the 85 percent removal goal at a slightly lower buffer concentration (500 ppm equivalent adipic acid) than during the adipic acid testing (640 ppm adipic acid). Theoretically, there should be little difference in the buffering capacity of the two. This difference could be explained by the fact that over the DBA test period, the average unit load was less than it was during the adipic acid testing. The poor performance observed for the TCA module over the period was due to the TCA spheres being badly distributed throughout the tower. Results of a brief test at a target of 95 percent $SO_2$ removal showed that approximately 1300 ppm DBA (measured as adipic acid) and a pH of 5.4 were sufficient to maintain the tray modules' efficiency above the target level. The results for the TCA showed a nearly equivalent performance; however, the unit's two fans were biased so that the tray tower treated more flue gas than did the TCA.

Although the required concentration of buffer in the scrubber slurry was less during the DBA testing, mass balance calculations showed that DBA was consumed at a higher rate than was adipic acid at equivalent scrubber operating conditions. To achieve 85 percent $SO_2$ removal at 75 percent unit load (146 MW), about 60 lb/hr (27 kg/hr) of DBA would be consumed, compared to 45 lb/hr (20 kg/hr) of adipic acid. This translates to about 15 lb of DBA fed per ton of $SO_2$ absorbed (7.5 g/kg), compared to 11 lb of adipic acid fed per ton of $SO_2$ absorbed (5.5 g/kg).

## ECONOMICS

Based on economic studies which TVA has performed (4), a 500 MW adipic acid enhanced limestone system is marginally more economical (0-5 percent lower annual cost) than a 500 MW conventional limestone FGD system. This indicates that site specific factors can obviously influence the selection of an adipic acid enhanced limestone system.

For the case specific to City Utilities' SWPP, the economics of three alternatives were considered to achieve 85 percent removal: (1) increasing the L/G in the tray tower, (2) addition of adipic acid, and (3) addition of DBA. The higher L/G option represents a capital cost intensive solution; whereas the adipic acid and DBA options have lower capital costs but higher

TABLE 5. DBA TEST RESULTS

| Test Period | Average Scrubber Feed pH | Average DBA Conc. (ppm as Adipic Acid) | Average $SO_2$ Removal, % |
|---|---|---|---|
| 85% $SO_2$ Removal | | | |
| Module S-1 | 5.4 | 480 | 90 |
| Module S-2 | 5.4 | 420 | 78 |
| 95% $SO_2$ Removal | | | |
| Module S-1 | 5.4 | 1310 | 96 |
| Module S-2 | 5.4 | 1020 | 94 |

annual operating costs. A present worth analysis was performed using escalation factors consistent with City Utilities' long range planning activities. The escalation of adipic acid (cost is ∿60¢/lb ($1.35/kg) in 1981 $) and DBA (cost is ∿30¢/lb (66¢/kg) in 1981 $) closely approximated C.U.'s assumed escalation rate of fuel oil, and the escalation of the cost of electricity (production costs only) closely approximated C.U.'s assumed coal escalation rate. The discount factor for the analysis was assumed to be equal to the projected general inflation rate.

The results of this study are shown in Figure 4. Note that the adipic acid option is a lower cost option than increased L/G for about 9 years. The technical uncertainties in making the L/G modification, the adipic acid system flexibility, and the large data base gathered make the adipic acid option a good choice. However, the DBA option remains the economic choice through more than 15 years. In fact, options for reducing the cost of DBA have not been fully investigated, so the cost may be less than that shown. Ease of handling the DBA solution is also a plus over solids handling, although care must be taken to keep the DBA solution above its crystallization temperature.

## CONCLUSIONS

Several conclusions concerning operation of a limestone FGD system with adipic acid can be drawn from this demonstration program:

- Adipic acid is a viable means for improving $SO_2$ removal in scrubbers which are limited from a dissolved alkalinity standpoint.
- The correlations from TCA prototype testing (Shawnee) predict full-scale results fairly well, but some conservatism should be used in design calculations.
- DBA is a technically viable alternative to adipic acid and is the economical choice at Springifeld City Utilities' Southwest Power Plant.

## INDUSTRIAL BOILER DEMONSTRATION

The main objective of this program was to demonstrate the effectiveness of adipic acid as an $SO_2$ removal enhancement agent in an industrial boiler limestone FGD system. The testing phase lasted a total of 30 days and was conducted in the natural oxidation mode of operation for the FGD system at the Rickenbacker Air National Guard Base (RANGB). As with the utility demonstration, a continuous $SO_2$ monitoring system was installed, certified, and operated according to published EPA specifications.

Another important objective of the program was to compare the economics of dual alkali and limestone-only FGD systems to an adipic acid enhanced limestone system for industrial boiler applications. The economic analysis was based on the results of the Shawnee testing (5,6,7) and a technology assessment report on FGD for industrial boilers (8).

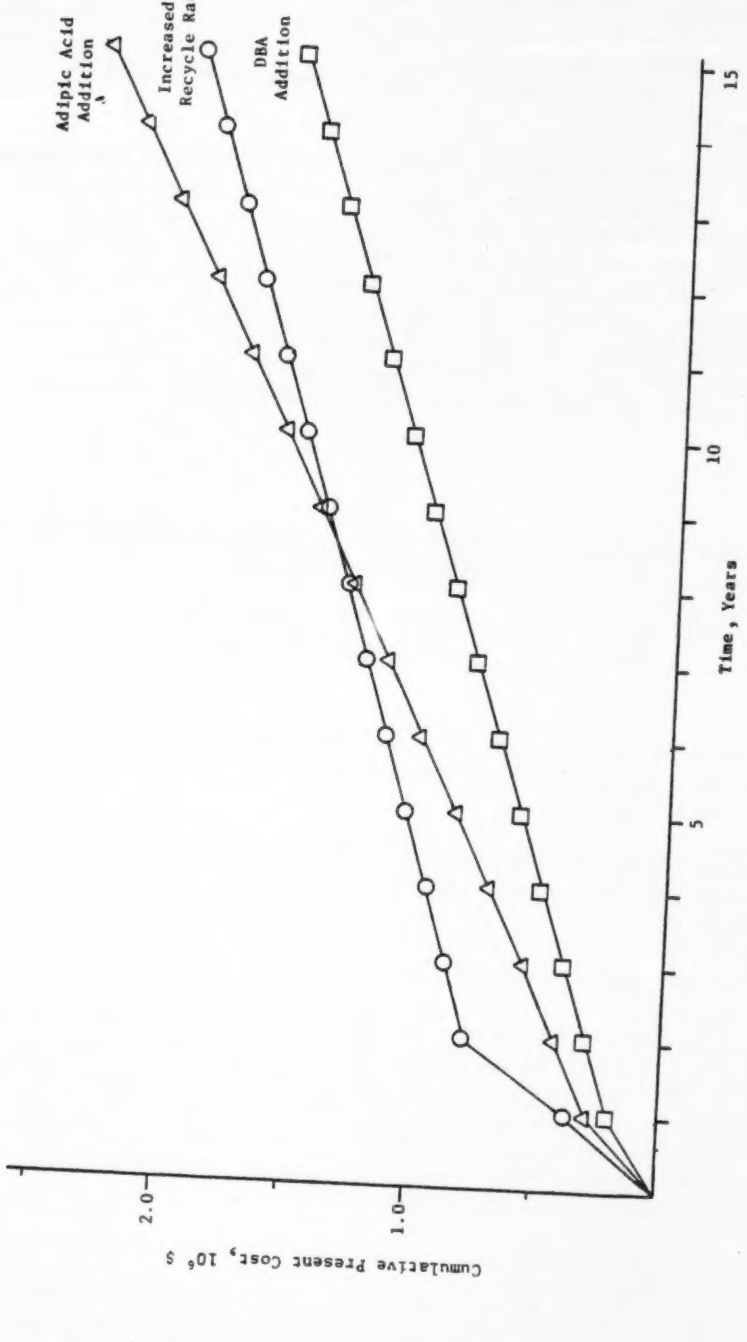


Figure 4. Comparison of alternatives for meeting 85 percent removal at Springfield.

## SYSTEM DESCRIPTION

The FGD system at Rickenbacker scrubs the flue gas from six stoker-fed coal-fired boilers. Five of the boilers are rated at a nominal 30 x $10^6$ Btu/hr (3.2 x $10^{10}$ J/hr), and the newest is rated at 60 x $10^6$ Btu/hr (6.4 x $10^{10}$ J/hr). Combustion air, supplied by forced draft fans, is controlled at 14 to 18 percent excess air. The average sulfur content of the coal was 2.6 percent during the testing, giving an average $SO_2$ emission rate from the boiler furnace of 4.94 lb $SO_2/10^6$ Btu (2120 ng/J) heat input.

The flue gas from the boilers was scrubbed by a Research-Cottrell/Bahco system designed for both particulate and $SO_2$ control. This unit was installed at the Base in 1974 and has been previously tested with both lime and limestone as the alkaline reagent (9,10,11). AB Bahco in Sweden developed this system. The unit at RANGE was the first application to coal-fired boilers; several systems have been used on foreign oil-fired industrial boilers.

Figure 5 is a diagram of the FGD system at RANGB. Flue gases from the six boilers are collected in a common manifold by an induced draft fan. Normal operating procedure involves maintaining a constant gas flow to the scrubber. This is accomplished by using a by-pass stack to infiltrate dilution air when the boiler flue gas output falls below a set volumetric rate. Gas flow is maintained by adjusting inlet louver dampers. A mechanical collector upstream of the fan removes large particulates from the gas. Because the gas flow is essentially constant regardless of the boiler load, changes in boiler load can significantly affect the inlet $SO_2$ concentration. The inlet value averaged about 700 ppm; however, values of 400 to 1000 ppm were often observed depending upon the number of boilers in operation.

Upon leaving the booster fan, the flue gas passes into the first stage of the scrubber. The gas is forced downward where it contacts mill pump liquid. The gas reverses direction, flowing upward. Entrained liquid falls out and is caught in the first stage carryover tray. The gas continues upward, impinging on the bottom of the second stage liquor reservoir. The gas travels upward around the second stage liquor reservoir and then reverses direction and is contacted with second stage liquor. Following another carryover tray, a bleed stream from the first stage carryover tray is used as thickener feed. Thickener overflow liquid is returned to the limestone feed tank, and thickener underflow is intermittently pumped to the sludge pond. When the underflow is not sent to the pond, it is fed to the scrubber for slurry solids control. No water is returned from the sludge pond to the system.

Makeup water is added at several points: (1) pump seal water; (2) water for lime slaking or limestone slurrying; and (3) flush water for scrubbing internals including mist eliminator wash (mist eliminator is washed while thickener underflow is being pumped to the pond).

Adipic acid was added in powder form to the limestone slurry tank through a vibratory screw feeder similar to the one used for the utility demonstration.

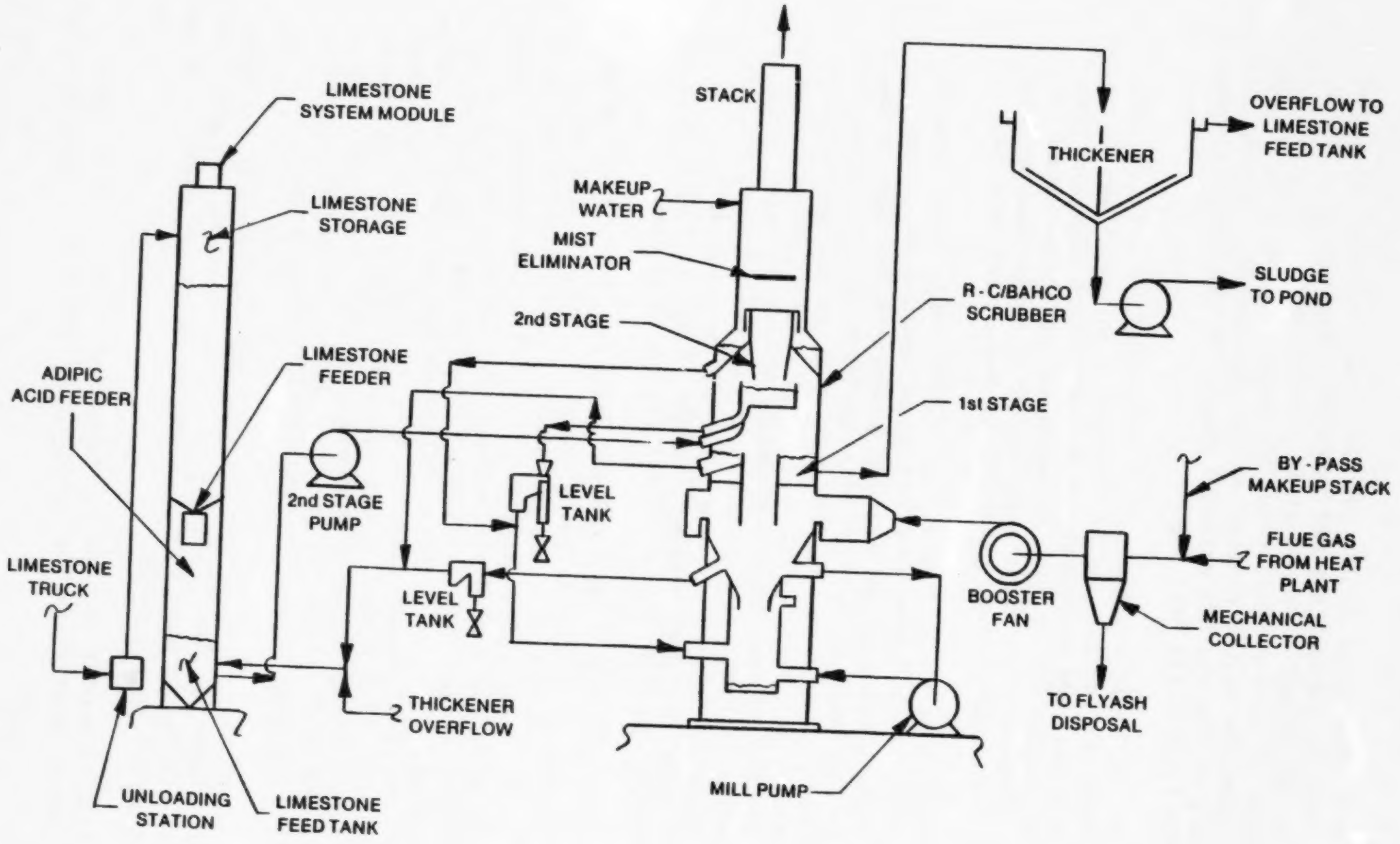


Figure 5. Research-Cottrell/Bahco FGD system at RANGB.

## TEST RESULTS

The RANGB FGD system has been tested in the past with both lime and limestone as the alkali reagent (12,13). Table 6 presents the results of these previous tests as well as those for the adipic acid testing (14). The adipic acid tests show a significant improvement in $SO_2$ removal compared to the limestone test (without adipic acid). The reliability* of the RANGB limestone FGD system was about 90 percent during tests both with and without adipic acid. During adipic acid testing, the reliability factor was 94.7 percent. The system was only down twice, once due to an electrical outage and the second time when foreign debris plugged the thickener underflow line. During the limestone (without adipic acid) test, the reliability was 91.4 percent, with several boiler and scrubber outages related mainly to severe weather problems.

TABLE 6. COMPARISON OF TEST RESULTS - $SO_2$ REMOVAL AT RANGB

| | Limestone | Lime | Limestone/Adipic Acid |
|---|---|---|---|
| Days of Testing | 42 | 29 | 30 |
| Max % Removal | 87.3 | 96.0 | 97.4 |
| Min % Removal | 51.0 | 86.6 | 90.0 |
| Avg % Removal | 65.8 | 91.5 | 94.3 |
| Avg Boiler Load, $10^6$ Btu/hr ($10^9$ J/hr) | - | 109 (115) | 101 (106) |

Limestone and adipic acid consumption during the program averaged 630 and 9.5 lb/hr (286 and 4.3 kg/hr), respectively. For an average concentration of adipic acid of 2000 ppm, the amount leaving the system in the thickener underflow averaged 9 lb/hr (4.1 kg/hr). If the water from the sludge pond was recycled (closed loop), the adipic consumption could be as much as 50 to 60 percent less. Analyses performed by PEDCo indicate that limestone utilization varied from 70 to 96 percent during the adipic acid testing.

## COST COMPARISON FOR INDUSTRIAL BOILER FGD SYSTEMS

As part of the demonstration program, an economic study was completed which compared the capital and annual costs for the following three FGD systems:

- Dual Alkali.
- Limestone.
- Limestone/Adipic Acid.

---

*Reliability = hours the scrubber operated divided by the hours the scrubber was called to operate.

The analysis compares the costs of the FGD systems for two model boiler sizes: 150 x $10^6$ Btu/hr (160 x $10^9$ J/hr) and 400 x $10^6$ Btu/hr (420 x $10^9$ J/hr) heat input. Costs for the dual alkali system are taken from the technology assessment report (15). Costs for the limestone and limestone/adipic acid systems were developed based on the Shawnee test data. The Rickenbacker FGD system was not used as a basis for this work because this system is not typical of new limestone FGD designs. The Shawnee TCA scrubber design was used instead because its size is typical of that for an industrial boiler and furthermore because it has been tested thoroughly with and without adipic acid.

Table 7 summarizes the capital investment and annual costs of the two limestone systems and a dual alkali system on the two model boilers. The data show that the capital investment for adipic acid enhanced systems are 5 to 6 percent lower than the base limestone system and the reduction in annual costs is about 2 to 3 percent lower for the adipic acid system. As stated in the technology assessment report, the dual alkali, lime, and limestone systems costs generally agree within 10 percent of each other (16). Although the accuracy of the cost data presented here is about ±30 percent, the relative cost difference between the adipic acid enhanced system and the base case limestone system is significant. The process configuration for each of these systems in identical, with differences being equipment size and (in one case) adipic acid feed system.

TABLE 7. COMPARISON OF FGD SYSTEM CAPITAL INVESTMENT AND ANNUAL COSTS FOR NEW INDUSTRIAL BOILERS (1978 DOLLARS)

| Boiler Size $10^6$ Btu/hr ($10^9$ J/hr) | FGD System | Capital Investment (\$1000) | Annual Cost (\$1000) |
|---|---|---|---|
| 150 (160) | Limestone | 1568 | 785 |
| 150 (160) | Limestone with Adipic Acid | 1488 | 765 |
| 150 (160) | Dual Alkali | 1657 | 778 |
| 400 (420) | Limestone | 2714 | 1435 |
| 400 (420) | Limestone with Adipic Acid | 2586 | 1412 |
| 400 (420) | Dual Alkali | 2576 | 1328 |

Several pieces of equipment in the limestone base design were reduced in size to reflect process advantages for the adipic acid enhanced system. Therefore, the capital investment difference is real even though the overall capital investment of the two systems is accurate to only ±30 percent. The difference in costs between the limestone and the dual alkali system, however, is not significant because of the large variation between the two process configurations.

## REFERENCES

1. Burbank, D. A., and S. C. Wang. "Test Results on Adipic Acid-Enhanced Lime/Limestone Scrubbing at the EPA Shawnee Test Facility--Second Report." In Proceedings: Fifth Industry Briefing on IERL-RTP Lime/Limestone Wet Scrubbing Test Programs (December 1979); EPA-600/9-80-032 (NTIS PB 80-199813). July (1980).

2. Burbank, D. A., and S. C. Wang. "Adipic Acid-Enhanced Lime/Limestone Test Results at the EPA Alkali Scrubbing Test Facility." EPA Technology Transfer Capsule Report; EPA-625/2-82-029 (in print). Prepared by Bechtel National, Inc. San Francisco, CA. May (1981).

3. Jarvis, J. B., et al. "Effect of Trace Metals and Sulfite Oxidation on Adipic Acid Degradation." Draft Final Report prepared for U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory. Prepared by Radian Corporation, Austin, Texas under Contract No. 68-02-3171, Task 29. July (1981).

4. Torstrick, R. L., C. D. Stephenson, and J. D. Veitch. "Economics of Limestone FGD Systems Using Adipic Acid." In Proceedings: EPA's Industry Briefing on the Adipic Acid Enhanced Limestone FGD Process (July 1981); EPA/IERL-RTP-1272 (Draft). October (1981).

5. Head, H. N., et al. "Recent Results from EPA's Lime/Limestone Scrubbing Programs--Adipic Acid as a Scrubber Additive." In Proceedings: Symposium on Flue Gas Desulfurization--Las Vegas, Nevada, March 1979; Vol. I, EPA-600/7-79-167a (NTIS PB 80-133168). July (1979).

6. Burbank, D. A., op. cit.

7. Burbank, D. A., et al. "Test Results on Adipic Acid Enhanced Limestone Scrubbing at the EPA Shawnee Test Facility--Third Report." In Proceedings: Symposium on Flue Gas Desulfurization--Houston, October 1980; Volume 1, EPA-600/9-81-019a (NTIS PB 81-243156). April (1981).

8. Dickerman, J. C., and K. L. Johnson. "Technology Assessment Report for Industrial Boiler Applications: Flue Gas Desulfurization." EPA-600/7-79-178i (NTIS PB 80-150873). November (1979).

9. Clarke, P. A., et al. "The Adipic Acid Enhanced Flue Gas Desulfurization Process for Industrial Boilers: Volume 1. Field Test Results." EPA/IERL-RTP-1335 (Draft). January (1982).

10. Howie, S. J. "Continuous Sulfur Dioxide Monitoring of the Industrial Boiler System at Rickenbacker Air Force Base." Columbus, Ohio. EPA Emissions Measurement Branch Report 80-IBR-6. March (1980).

11. EPA/IERL-RTP. "Capsule Report - Bacho Flue Gas Desulfurization and Particulate Removal System." EPA-625/2-79-022. July (1979).

12. PEDCo Environmental, Inc. "Continuous Sulfur Dioxide Monitoring of the Industrial Boiler System at Rickenbacker Air Force Base." Columbus, Ohio. EPA Emissions Measurement Branch Report 79-IBR-2. August (1979).

13. Howie, S. J., op cit.

14. Clarke, P. A., op cit.

15. Dickerman, J. C., op cit.

16. Dickerman, J. C., op cit.

# COMMERCIAL APPLICATION EXPERIENCE WITH ORGANIC ACID ADDITION AT CITY UTILITIES OF SPRINGFIELD

by: N. D. Hicks, P.E.
Power Plant Manager

D. M. Fraley
Environmental Results Specialist

City Utilities
Springfield, Missouri 65801

## ABSTRACT

During 1981, Southwest Power Station participated with Radian Corporation and EPA in commercially testing adipic acid as an additive to enhance the effectiveness of its limestone flue gas desulfurization (FGD) system. After successfully demonstrating the effectiveness of adipic acid, a short test run was conducted using dibasic acids (DBA).

Efforts were underway to develop a long-range improvement program to enhance the efficiency of the FGD system with the following options being considered: a) increase the Liquid/Gas ratio of the recycled slurry in the TCA's; b) convert the TCA's to open spray towers and increase the L/G ratio; c) utilize the TCA's (with stainless trays) in conjunction with the use of adipic acid; and d) utilize DBA instead of adipic acid.

In the final analysis, it was decided to use DBA with adipic as a backup system.

Since December, 1981, a temporary DBA storage and feed system has been in service. Because of the effects of cold weather on the crystallization of the material, handling problems have been encountered. But its effectiveness as a buffer in the limestone FGD system has been proven. A permanent material storage and feeding system is currently under design.

# INTRODUCTION

Southwest Power Station Unit 1 is a 194 MW fossil fueled unit owned and operated by City Utilities of Springfield, Missouri. The unit was designed by Burns & McDonnell. Commercial operation of the generating unit began in May, 1976 while the FGD Systems were not declared operational until September 1977.

The steam generator was supplied by Riley Stoker Corporation and was designed to burn high (3.5 to 4.5 percent) sulfur coal. Air Correction Division of Universal Oil Products (UOP) furnished and installed the electrostatic precipitator and the two-module flue-gas scrubber. Each absorber module consisted of a presaturator area; three TCA beds, each containing spheres to enhance gas-liquid mixing; two chevron mist eliminator banks; and a reaction hold tank. A common limestone preparation area and sludge dewatering train serve both modules. The design was based on a limestone composition of 98.7 percent $CaCO_3$, 0.7 percent $MgCO_3$, and 0.6 percent inerts.

The attached Figure 1 presents the process flow diagram. Basically, the induced draft (ID) fans pull the flue gas from the boiler through the air heaters and the electrostatic precipitator (ESP) and discharge into the scrubber inlets. Particulates (fly ash) are removed from the flue gas by the ESP and conveyed to dry storage. $SO_2$ removal is achieved in the scrubber with waste products of the reaction removed by continuous outflow from the scrubbers to a thickener tank. The thickener separates the waste solids from the aqueous supernatant, which is subsequently recycled to the scrubber system. The waste solids are drawn from the thickener and passed across a travelling vacuum belt for further removal of water. The dewatered sludge, having a solids content of about sixty percent, is then mixed with dry fly ash to produce a fixed material which is landfilled on site.

Limestone is prepared for the scrubbing process by wet grinding in two (2) ball-tube mills. There is presently no classification of the ballmill outputs, so fineness of grind cannot be readily controlled.

In 1980, Radian Corporation and City Utilities (C.U.) entered into an agreement to participate in a demonstration project to be sponsored by EPA's Industrial Environmental Research Laboratory. Adipic acid was to be tested as a buffering agent in the Southwest Unit 1 limestone scrubber to

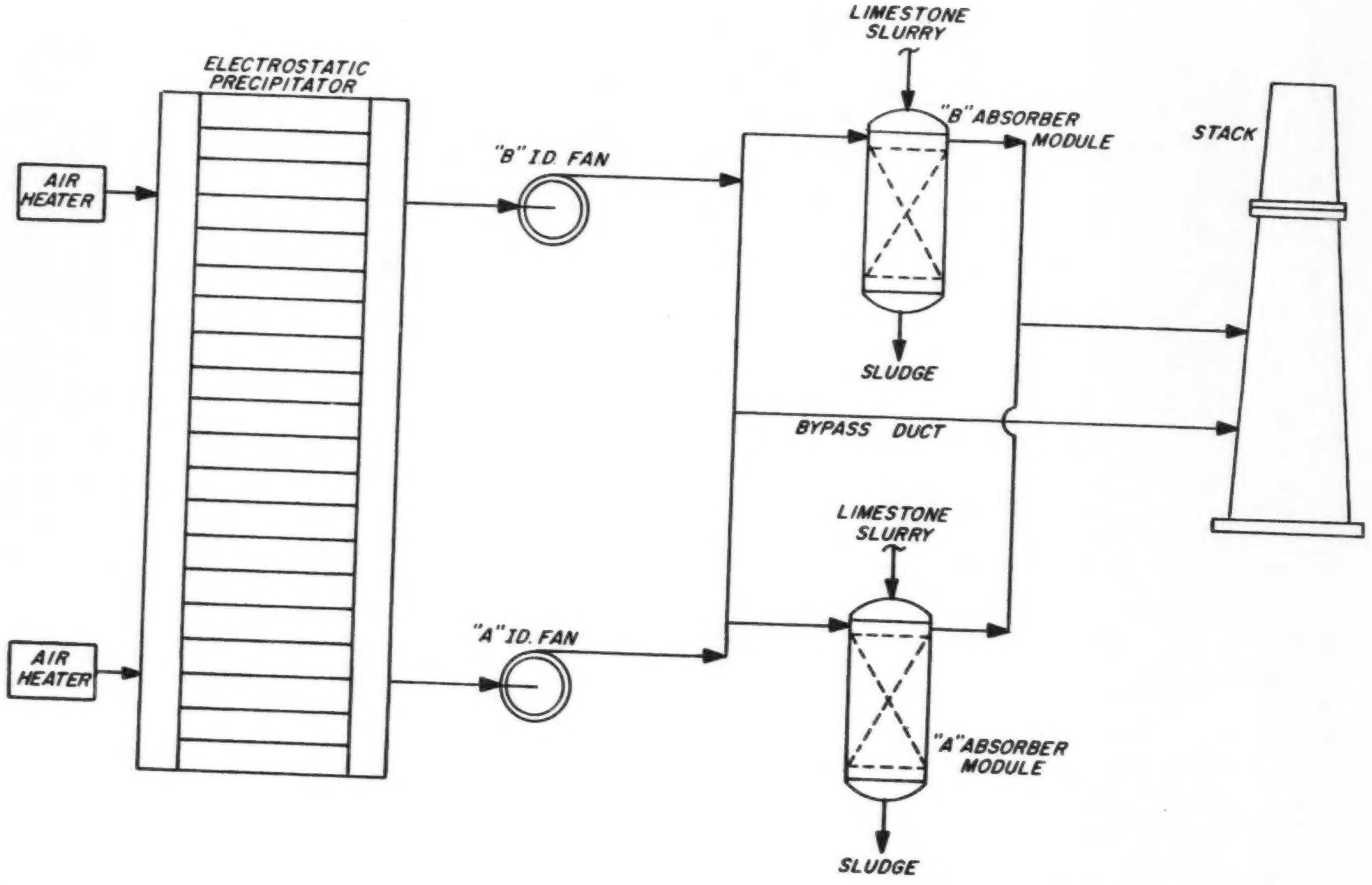


FIGURE 1 SOUTHWEST UNIT 1 PROCESS FLOW DIAGRAM

determine its effectiveness in increasing limestone utilization and $SO_2$ removal. This testing was conducted during 1981 and did verify the effectiveness of adipic in a commercial limestone scrubber.

Near the end of the nine-month testing program, a short test-run was conducted using dibasic acid (DBA) instead of adipic. DBA is actually a by-product of adipic acid manufacturing and is composed primarily of glutaric, succinic, and adipic acids. It was felt that DBA would provide essentially the same buffering effects as adipic but with less material expense. Test results obtained by Radian during a one-month test verified the effectiveness of DBA.

## SYSTEM IMPROVEMENT ALTERNATIVES

City Utilities participated with Radian in the EPA test program because of our desire to improve the effectiveness of the scrubber operation. Through discussions with UOP, it appeared that several options might be suitable for consideration in C.U.'s efforts to improve the reliability and efficiency of the scrubbers.

During early phases of the Radian test program, it was decided that the availability of the scrubbers had to be improved. The failure of spheres in the TCA necessitated the removal of a module from service monthly to clear failed spheres and resulted scale and pluggage from the absorber. This generally required one week per module which was expensive in terms of availability, maintenance manpower, and sphere consumption.

The evaluation of this problem led to discussions with representatives of several firms. During a discussion with Babcock and Wilcox personnel, it was suggested that stainless steel diffusion trays be considered for replacement of the TCA spheres. Upon more thorough investigation of this idea, C.U. purchased stainless (317 L +) trays with nominal one-inch (1") perforations from UOP and installed them in place of the spheres and cages in May, 1981. The trays required minor modifications during the initial period of operation. Since that time, however, they have substantially enhanced the availability of the S-1 module. In October, 1981, a similar conversion was made in the S-2 module, thus eliminating the trouble-prone spheres altogether. While the use of stainless trays has considerably improved the availability of both modules, no improvement was noted in $SO_2$ removal efficiency as a direct result of this conversion. The replacement of the spheres was justified economically by the fact that the trays installed had an economic pay-out of one (1) year when compared to the annual replacement and maintenance costs associated with the spheres. This has been verified in the operation of the S-1 module during the past year.

### ADIPIC ACID ADDITION TO TRAY TOWER

By participating with Radian in the EPA test program, C.U. had witnessed the effectiveness of adipic acid in improving the $SO_2$ removal efficiency of its scrubbers. In evaluating the use of adipic as a long-term operating alternative, the question was not "will it work?" but "can we afford it?" At a 1981 cost of $0.60 per pound, adipic acid would be an expensive additional operating cost. But a minimal capital outlay would be required to establish a permanent adipic storage and feed system.

## DIBASIC ACID ADDITION TO TRAY TOWER

As with adipic, C.U. had witnessed for a short period of time the effectiveness of DBA in its scrubber system. The DBA was easy to handle and provided the utmost in flexibility of scrubber operation. So again, the question was economics. At $0.30 per pound dry weight, the DBA seemed to be advantageous over adipic although DBA was projected to be only 85 percent (%) as effective as adipic, pound for pound. The capital outlay for a DBA storage and feed facility was estimated at $150,000 to $175,000.

## INCREASE L/G IN TRAY TOWER

Another possible way of improving the $SO_2$ removal efficiency of the scrubbers was to increase the recycled liquid rate relative to the flue gas flow ratio (L/G) in each module. The design L/G for the TCA's was 40 gal/acf. By today's standards this value is quite low. By redesigning and rebuilding the slurry pump discharge piping and header systems, both recycle pumps in each module could be operated simultaneously, providing a theoretical L/G of 75 to 80. The full-time utilization of all four recycle pumps would have eliminated the redundancy of the recycle system. The capital cost estimate for this option was placed at $500,000 to $600,000 per module with no allowance for the purchase of additional pumps.

## CONVERT MODULES TO SPRAY TOWERS

The elimination of the trays in the absorber was discussed with UOP as an option that would provide the most maintenance-free absorber possible. But the design velocity through the absorber was quite high, about 13 FPS, which rendered the likelihood of successful performance quite marginal. The estimated modification cost per module was in the range of one million dollars.

## ALTERNATIVE SELECTED FOR LONG-TERM OPERATION

City Utilities officials, after considering the long-term options available to them for improving the scrubber operation, decided on a course of action that would immediately initiate the use of DBA through a temporary storage and feed system with adipic acid retained as a back-up additive. This decision was based on the following factors:

a. The use of DBA or adipic would provide the quickest means by which the scrubber operating efficiency could be improved.

b. No additional downtime of the generating unit beyond normal maintenance outages would be needed to install permanent DBA system equipment.

c. Other alternatives proposed involving major physical modifications provided purely theoretical efficiency improvements, whereas DBA and adipic had been tested and efficiency gains verified.

d. DBA appeared to possess the most favorable economics of the alternatives evaluated.

It was quite important to C.U. officials that improved scrubber operating efficiencies be obtained immediately. In late 1980, Region VII of the Environmental Protection Agency cited the operation of Southwest Power Station Unit 1 for failure to comply with flue gas emission regulations. By October 1981, upon completion of Radian's testing, plans for a temporary DBA storage and feeding system were being implemented.

## DBA ENHANCED SYSTEM OPERATION

In December, 1981 a temporary DBA system was put into service as shown schematically in Figure 2. The storage vessel was a leased 6,000 gallon tank truck, insulated, and with surface heating coils. The temporary heating system consisted of two 5,500 watt electric hot water heaters in series on a closed loop system to the truck heating coils. All piping was heat-traced and insulated.

DBA was received from the vendor by truck as a twenty (20%) percent solution. The crystallization temperature at this concentration was about 75° F. The crystallization temperature for an 80% solution was about 185° F. As can be seen, temperature control during winter operation was extremely critical.

### OPERATING PROBLEMS

With winter temperatures of -15° F, crystallization problems were encountered. The temperature recovery capability of the temporary heating system was marginal at best as its primary purpose was to sustain a certain temperature. The major problems occurred due to incoming shipments arriving at temperatures of 40 or 50° F, well below the threshold of crystallization. This presented difficulties in offloading the material from the trucks. Inside the storage vessel the temperature recovery of the newly added liquid was so slow that the material would crystallize and plug the discharge piping. When the DBA system was forced out of service, adipic was added to the system to sustain the desired scrubber operating efficiency.

Another weather related problem involved the sludge dewatering and mixing facilities. The sludge-fly ash mixer and the transporting conveyors are not protected from the weather, and were thus prone to freeze-ups. When this occurred, the settled solids were periodically drained from the bottom of the thickener vessel in a slurry state with no recovery of the entrained liquid containing the DBA. This resulted in a substantial waste of DBA.

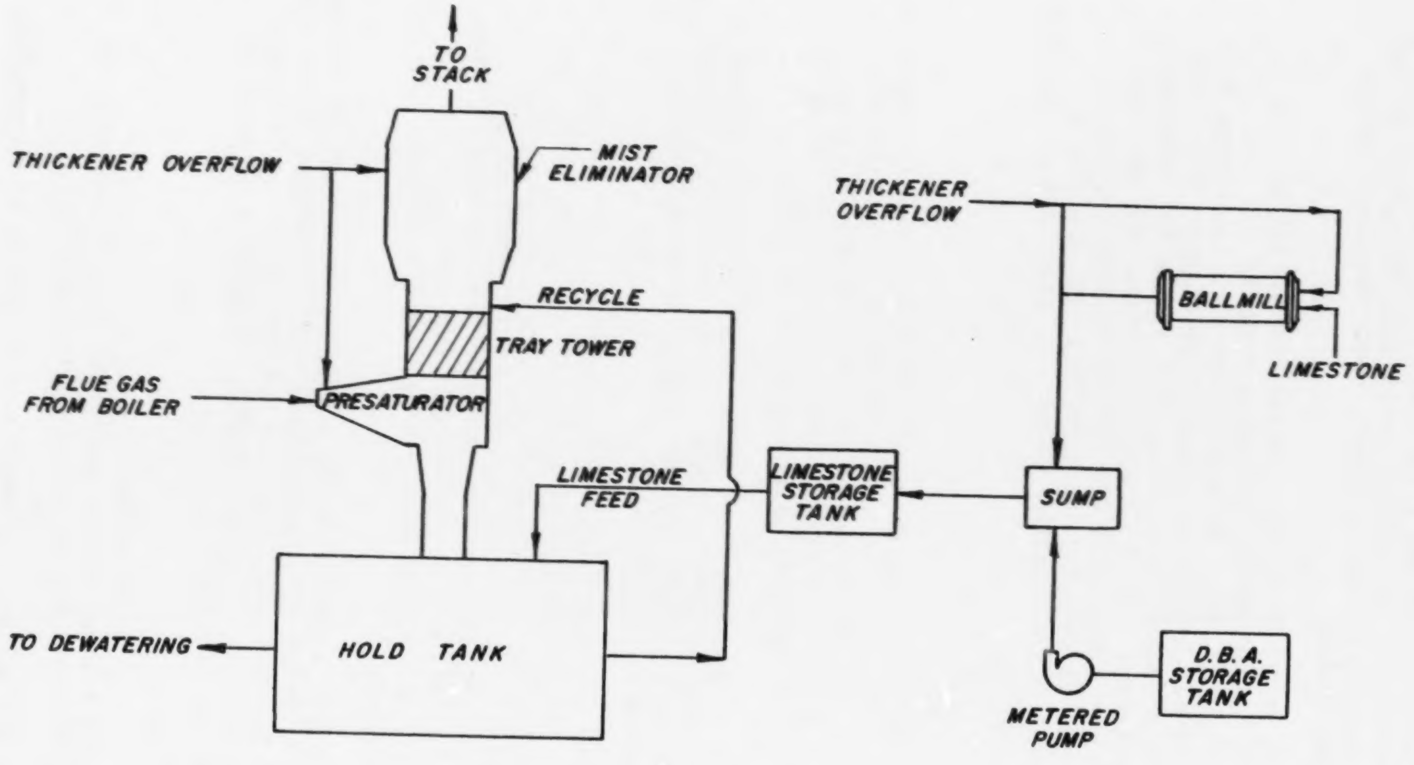


FIGURE 2 SCRUBBER FLOW SCHEMATIC WITH D.B.A.-TEMPORARY SYSTEM

As our storage capacity of DBA was quite limited, delivery scheduling was both critical and difficult. On several occasions, the supply of DBA was exhausted before receiving another shipment, requiring supplemented adipic to be added to the system.

The inherent design of this temporary system limited the ability to optimize DBA usage. The DBA was added, through a manually operated control valve, to the limestone slurry tank. Make-up to the scrubber system from the slurry tank is determined through an automatic pH control loop. The pH can be controlled individually for each scrubber system but individual DBA control cannot be attained with the temporary system. The DBA concentration in the limestone slurry tank has varied drastically, due in part to the manual control valve being inadvertently left open for a prolonged period of time. Overall system flexibility could not be obtained with the temporary DBA system.

## SYSTEM EFFECTIVENESS

Figure 3 presents the effectiveness of DBA at a pH of 5.4 in enhancing the $SO_2$ removal in C.U.'s limestone scrubber. Data for this curve was obtained during a period when the liquid systems were maintained in a tightly closed loop. As was previously discussed, closed loop operation was not always the case from December 1981 through March, 1982.

The use of DBA has allowed the plant to utilize alternative sources of coal. Test burns of coal with up to seven (7%) percent sulfur content have taken place since January 1982. By increasing the concentration of DBA, compliant operation was achieved.

The DBA useage rate has been higher in the December 1981 through March 1982 period than that documented by Radian in September 1981. Instead of 15 lb. of DBA per ton of $SO_2$ absorbed, it has averaged about 20 lb., or a 40% increase. This can be accounted for in part by the inability to operate in a closed-loop made during a portion of the period and the burning of test coals with drastically higher sulfur content. Because of these variations, any attempt to provide sound economic data at this time would be premature.

Even with the problems inherent in the temporary DBA system, by having the backup capability of using adipic, Southwest Unit 1 operated during the first quarter of 1982 in compliance with flue gas emissions regulations. The quarterly average emission rate was 1.0 lbs. $SO_2$/MBTU as compared to the regulated value of 1.2 lbs./MBTU.

## PERMANENT DBA SYSTEM

The attached Figure 4 shows schematically the planned permanent DBA system. The system would have the following major elements.

a. storage - 30,000 gallons, expandable if necessary to accommodate future shipping and material availability trends.

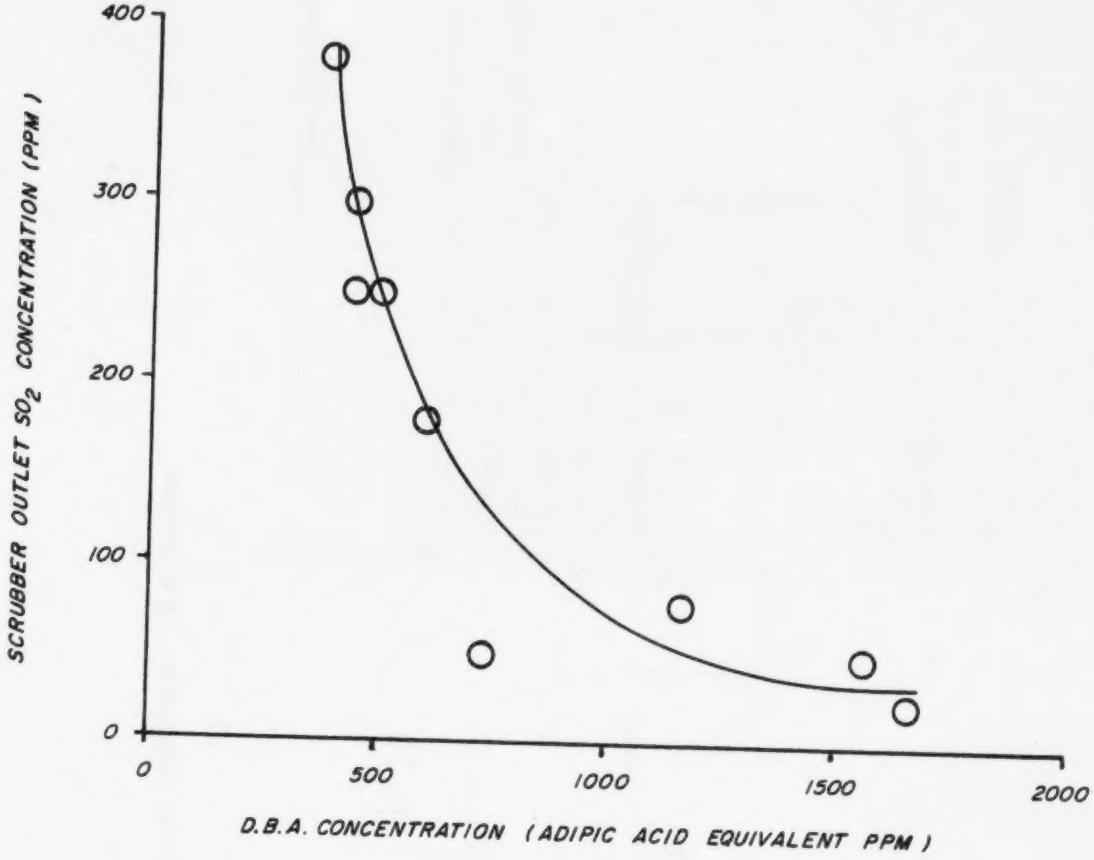


FIGURE 3 SCRUBBER OUTLET $SO_2$ CONCENTRATION V.S. DBA CONCENTRATION.

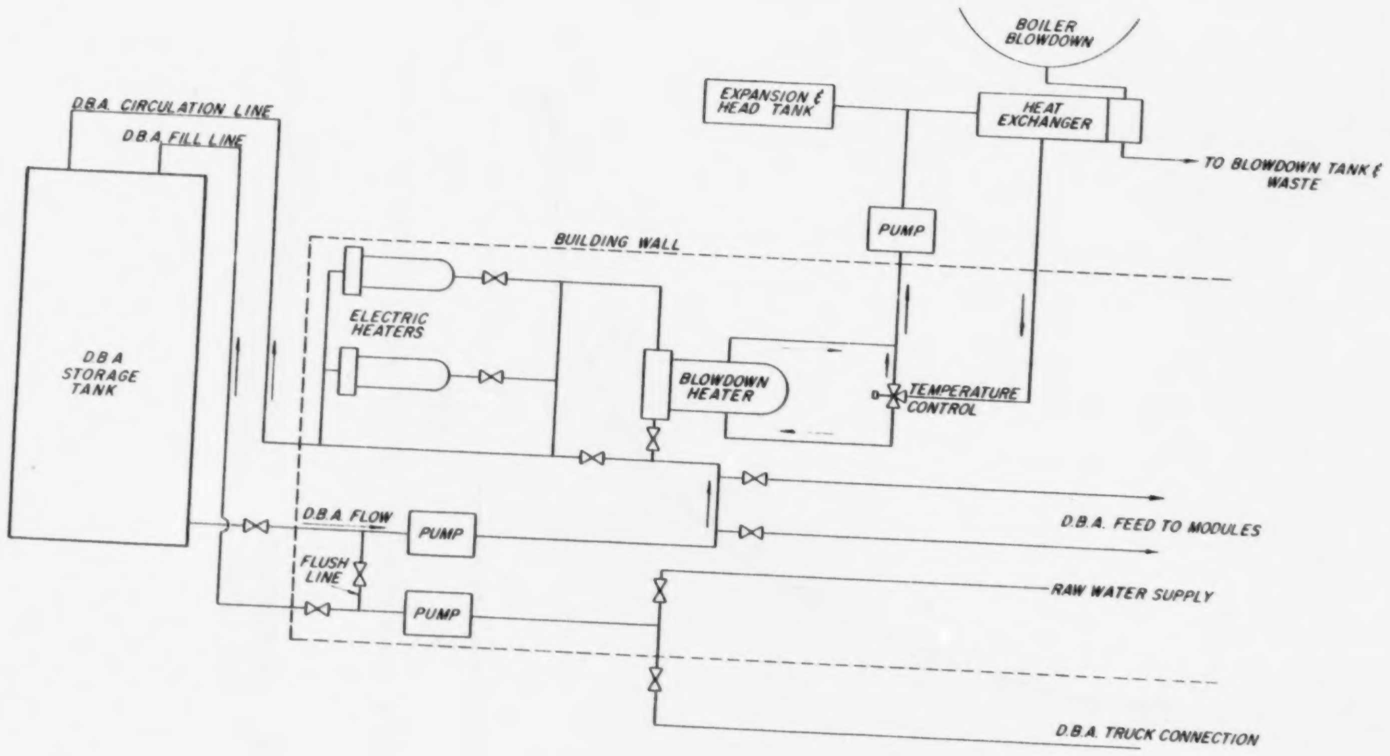


FIGURE 4 SCHEMATIC- PROPOSED PERMANENT D.B.A. SYSTEM

b. heating system - continuous recirculation system with heat exchangers mounted externally to the storage tank for better maintainability. Electric heaters would be used when the unit could not supply steam; otherwise waste steam would be used to maintain system temperature.

c. material feed system - individual material feed to each scrubber system to allow the operator to fine-tune the system for most efficient operation.

The estimated cost of installing this system is about $220,000. Gains in the control of DBA useage should provide savings in DBA consumption which would pay for the installation in approximately five years. The flexibility of control provided by this system would provide a quicker response to an operating abnormality so that periods of excess emissions could be minimized.

## CONCLUSIONS

City Utilities has evaluated several alternatives for improving the scrubber operation at its Southwest Power Station Unit No. 1. Selected as the most viable and economic alternative is a system utilizing DBA with adipic acid as a standby material.

C.U. is committed to the program selected and intends to closely monitor the effectiveness and economic trends of DBA operation in the coming months. Nothing so far that has been observed has caused any doubt as to the decisions that have been made. DBA does significantly enhance the operating efficiency of C.U.'s limestone scrubbers and provides the least expensive alternative for obtaining compliant operation of Southwest Unit 1.